(54) Title: POLYMER GRID TRIODES

(57) Abstract

Polymer grids comprising a body of electrically conducting organic polymer (3), which body has an open and porous network morphology, and presents an expanded surface area void-defining porous network (3) are disclosed. In most applications active electronic material (2, 4) is located within at least a portion of the void spaces defined by the porous network (3). These grids are advantageously incorporated into polymer grid triodes and especially light-emitting polymer grid triodes.

POLYMER GRID TRIODES

Technical Field

This invention relates generally to polymer grids, to methods for fabricating such polymer grids and to uses for such polymer grids in electronic devices such as polymer grid triodes and light-emitting polymer grid triode structures.

Background Art

Prior to the invention of the transistor, vacuum tube triodes were the principal three-terminal devices used in active electronic circuits. The vacuum tube triode comprises three electrodes:

(i) A cathode where electrons are emitted by thermionic emission;

(ii) An anode where the electrons are collected;

(iii) An open grid placed in the vacuum tube between the cathode and the anode.

Typically a voltage is applied between the anode and the cathode with the anode positive with respect to the cathode such that current flows from anode to cathode (electrons flow from cathode to anode). A bias voltage is applied to the grid with respect to the cathode; typically a high impedance voltage source is used so that the grid does not draw significant current. In this way, a relatively small grid-cathode voltage can be used to control the current between the cathode and the anode, a key feature in the use of such triodes in amplifier circuits, oscillator circuits, control circuits and the like.

The transistor, in its various forms, is also a three-terminal device; a solid state analogue of the triode. The transistor does not utilize a grid to

control the current in the external circuit; such
control is obtained by other means. For example, in a
field effect transistor (FET), the source-drain current
is controlled by the gate voltage; application of a
gate voltage creates carriers in the source-to-drain
channel and renders the channel conducting. Thus, an
FET is an active three-terminal device, the gate
voltage controls the source-drain current. An npn
transistor is, fundamentally, two pn junction diodes
back-to-back. Again, an npn transistor is a three-
terminal device; by controlling the bias of the two
diodes independently through contact to the center p-
type layer, one can control the current between the two
n-type layers and thereby achieve gain (S.M. *Sze,
Physics of Semiconductor Devices* (Wiley, New York,
1981).

In the FET, as well as in transistors in other
forms, the frequency response is limited by the size of
the device. For example, FETs with large
source-to-drain spacing will be slow relative to FETs
with a smaller source-to-drain spacing. The response is
limited by the time required for the carriers to travel
from source to drain. Thus, modern semiconductor
technology strives for the following:

(a) Ever smaller devices, for example with
sub-micron resolution, thereby achieving more circuits
per unit area and higher frequency response;

(b) Higher mobility materials so as to reduce the
time required for the carriers to travel from source to
drain.

It is well known that there is considerable cost
and technical difficulty involved in the fabrication of
such sub-micron transistors and arrays of such
transistors (integrated circuits) using high mobility
single crystal materials.

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The semiconductor on-chip technology that is the heart of modern electronics is not appropriate to certain important electronic applications. An example is the active matrix liquid crystal display. In order to achieve the desired contrast in a liquid crystal display, it is desirable to have each pixel of the display controlled by a transistor. In the active matrix liquid crystal display, it is advantageous to fabricate these control transistors as thin film transistors on a surface which is an integral part of the display. The technology is limited by poor yields, high costs and poor high frequency response (low speed operation), all of which result from the need to use conventional transistor design with the low mobility materials amenable to thin film deposition on surfaces (for example, amorphous silicon, organic semiconductors and the like).

Thus, there is a need for improved low cost three-terminal solid state devices, analogous to the vacuum tube triode and to the transistor, which can be easily manufactured, and which utilize low mobility materials in a configuration where the cathode to anode distances are submicron.

There is also a need for new concepts in the area of electroluminescent devices. Recently, light-emitting diodes (LEDs) fabricated with conducting polymers (H. Burroughes, D.D.C. Bradley, A.R. Brown, R.N. Marks, K. Mackay, R.H. Friend, P.L. Burns and A.B. Holmes, Nature 347, 539 (1990); D. Braun and A.J. Heeger, Appl. Phys. Lett. 58, 1982 (1991)) have attracted attention due to their potential for use in display technology. Such LED's are layered structures with two electrodes separated by charge transporting and luminescent layers. Among the promising materials for use in polymer LEDs are poly(2-methoxy-5-(2'-ethyl-hexyloxy)-1,4-phenylene vinylene), MEH-PPV, a

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semiconducting polymer with energy gap E_g ~ 2.1 eV (U.S. Patent No. 5,189,136) and poly(2,5-bis(cholestanoxy)-1,4-phenylene vinylene) (BCHA-PPV), a semiconducting polymer with energy gap E_g ~ 2.2 eV (United States Patent No. 5,189,136). Both MEH-PPV and BCHA-PPV are soluble in common organic solvents, thereby enabling relatively simple device fabrication by processing the active layer from solution. In the polymer LEDs the semiconducting polymer is sandwiched between two electrodes; a low-work function metal (such as Ca, Al, and the like); and a transparent electrode, such as indium/tin oxide (ITO) (D. Braun and A.J. Heeger, Appl. Phys. Lett. 58, 1982 (1991)). By using a conducting polymer, such as polyaniline (PANI) (rather than indium/tin-oxide, ITO) as the hole-injecting contact, robust and mechanically flexible LEDs have been prepared (G. Gustafsson, Y. Cao, G. M. Treacy, F. Klavetter, N. Colaneri, and A.J. Heeger Nature, 357, 477 (1992)).

Electroluminescent (EL) devices utilizing small organic molecules as the luminescent semiconducting species were well known and extensively developed prior to the discovery of light-emitting diodes made with conjugated polymers. See, for example, the following: C.W. Tang, S.A. Van Syke, Appl. Phys. Lett. 51, 913 (1987); C.W. Tang, S.A. Van Syke and C.H. Chen, J. Appl. Phys. 65, 3610 (1989); C. Adachi, S.Tokito, T.Tetsui and S. Saito, Appl. Phys. Lett. 55, 1489 (1989); C. Adachi, S.Tokito, T.Tetsui and S. Saito, Appl. Phys. Lett. 56, 799 (1989); M. Nohara, M. Hasegawa, C. Hosohawa, H. Tokailin, T. Kusomoto, Chem. Lett. 189 (1990). In the small molecule EL devices of the prior art, the active layers are typically deposited using vacuum deposition. Transport layers (both electron transport layers and hole transport layers) were developed to improve the carrier injection

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and to balance the injection of electrons and holes so as to achieve higher efficiency.

Unfortunately, EL devices made with organic and/or polymeric materials as the semiconducting and luminescent materials suffer three important drawbacks that impede large-scale applications:

i) Emission of light at the desired brightness levels often requires the application of a relatively high voltage.

ii) The external conversion efficiency is low.

iii) Brightness is limited, particularly at voltages below 5 volts.

Recent progress has shown that by generalizing to heterojunction devices which include an electron transport layer, device efficiency can be somewhat improved in polymer LEDs using, for example, BCHA-PPV (C. Zhang, S. Hoger, K. Pakbaz, F. Wudl and A. J. Heeger, J. Electron. Mater. 22, 745 (1993)) or using a soluble cyano-derivative of poly(phenylene vinylene), PPV (N.C. Greenham, S.C.Moratti, D.D.C. Bradley, R.H. Friend, A.B. Holmes, Nature, 365, 628 (1993)).

Nevertheless, general and broad needs still exist for device concepts that result in light-emitting structures with increased efficiency, decreased turn-on voltage, and increased brightness.

Disclosure of Invention:

We have now discovered a polymer grid which can be advantageously incorporated into electronic devices as either an active or passive element. This polymer grid is made up of a body of electrically conducting organic polymer. This body has an open and porous network morphology and defines an expanded surface area void-defining porous network. In certain embodiments an active electronic material is located within at least a portion of the void spaces defined by the porous

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network. This polymer grid may be incorporated into electronic devices where the grid, as an active or passive element, can affect the transport of electrons or holes through the material of the device. The polymer grid has been shown to affect electronic performance and light emission both in the case where the grid is an "active" element connected to an external circuit and in the case where it is a "passive" element not specifically connected to an external circuit.

Thus, by the use of this grid one can achieve polymer grid triodes comprising three electrodes. The first and second electrodes in either order, are analogous to the anode and/or cathode of the vacuum tube triode. The polymer grid, either as a passive element or electrically connected to serve as a true third electrode, is located between the first two electrodes and is analogous to the grid electrode of the vacuum tube triode.

One or more active electronic materials may be placed between the first electrode and the polymer grid, within the polymer grid, or between the polymer grid and the second electrode. Charge carriers are injected from the electrodes into the active electronic materials. This charge carrier injection may be either single-carrier injection (for example, hole injection into otherwise filled energy states) at one electrode or two-carrier injection (hole injection into otherwise filled energy states at one electrode and electron injection into otherwise empty states at higher energy at a second electrode).

The active materials serve to transport the electronic charge carriers, the carriers being affected, and in some embodiments controlled, by the polymer grid. The active electronic materials, which transport electronic charge carriers between the first

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and second electrodes are conductors with various
levels of electrical conductivity, one or more of which
can be, for example, semiconductor materials.

5   In an additional aspect the polymer grid may be
incorporated into light-emitting devices to provide
light-emitting polymer grid triodes comprising three
electrodes. In these triodes one or more of the active
materials which are present and serve to transport the
electronic charge carriers are semiconducting and
10   luminescent materials, thereby leading to radiative
recombination of electrons and holes and the emission
of light. In these devices the transport of carriers
and thus the emitted light can be controlled and
affected by the polymer grid.

15   As previously noted, the polymer grid may be an
active (that is electrically connected) or passive
element of these devices. As a passive element, the
grid can increase the efficiency of devices
dramatically. Although not understood with certainty,
20   it appears that the polymer grid's high surface area
network enhances the local electric field upon the
application of a voltage between the first and second
electrodes, resulting in enhanced charge carrier
injection into one or more of the active electronic
25   materials. In the case of light-emitting devices, the
polymer grid enhances the local electric field
sufficiently that on applying a voltage between the
first and second electrode, charge carriers are
injected and light is emitted.

30   In another embodiment, the polymer grid is
electrically connected so as to provide a third
electrode of a "triode" configured device In this case
the polymer grid is electrically connected to an
external circuit such that a voltage can be applied to
35   the polymer grid as an electrode, and current can be
drawn in the grid circuit, either positive or negative,

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between the polymer grid electrode and one of the other two electrodes so as to function as a three-terminal polymer grid triode.

It is additionally an aspect of the present invention to provide light-emitting polymer grid triodes with two-carrier charge injection in which the polymer grid electrode is electrically connected to an external circuit such that a voltage can be applied to the polymer grid electrode and current can be drawn in the grid circuit, either positive or negative, between the polymer grid electrode and one of the other two electrodes so as to function as a three-terminal light-emitting polymer grid triode.

It is an additional aspect of the present invention to provide two-carrier polymer grid triodes. In these devices the electron and hole currents can be controlled and balanced by biasing the polymer grid electrode or by including two or more independent polymer grid electrodes, separated by an active layer, that can be separately biased with respect to the anode and the cathode, respectively.

It is an additional aspect of the present invention to provide polymer grid triodes and light-emitting polymer grid triodes in which the various layers are thin films. With such configurations, the total distance between the first and second electrodes is set by the thickness of the films in a vertical configuration. This makes possible polymer grid triodes and light-emitting polymer grid triodes with sub-micron dimensions between the anode and cathode.

In a further aspect this invention provides processes for forming the polymer grids. In these methods, blends are formed of the conductive organic polymer which makes up the polymer grid with a sacrificial host polymer. The two polymers exist in the blend as bicontinuous interpenetrating phases.

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When the host polymer is removed, such as by sublimation, dissolving, or the like, the desired polymer grid is formed. Active material may be placed in the voids of the grid as the host polymer is being

5   removed or thereafter.

Brief Description of the Drawings

This invention will be further described with reference being made to the accompanying drawings in which the figures show the following:

10   Fig. 1 is a schematic, not-to-scale cross-sectional view of a polymer grid triode.

Fig. 2 depicts the electronic structure of an Al/MEH-PPV/PANI-CSA/MEH-PPV/Ca polymer grid triode under various bias conditions with 2A being the

15   structure under zero-bias condition; 2B being the structure under flat-band condition; 2C being the structure under turn-on condition; and 2D being the structure under cut-off condition.

Fig. 3 depicts the electronic structure of an

20   Au/P3OT/PANI-CSA/P3OT/Au polymer grid triode under various bias conditions with 3A being the structure under zero-bias condition; 3B being the structure under flat-band condition; 3C being the structure under turn-on condition; and 3D being the structure

25   under cut-off condition.

Fig. 4 is an absorption spectrum derived in Example 1 of a mixture of a conductive polymer and a host polymer useful for preparing a polymer grid, before and after the host polymer is removed and

30   replaced with an active electronic material.

Fig. 5 is a graph of the electrical conductivities of various conductive polymer/host polymer blends as measured in Example 3.

Fig. 6 is a series of graphs generated in Example

35   4 showing current vs voltage characteristics for

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devices containing polymer grids fabricated from
different blends of conductive polymer and host
polymer.

5   Fig. 7 shows the external quantum efficiency (QE)
of the polymer grid light-emitting structure as a
function of the fraction of conductive polymer in the
initial conductive polymer/host polymer blends as
measured in Example 5.

10   Fig. 8 shows the brightness of the polymer grid
light-emitting structure at 4 volts forward bias as a
function of the fraction of conductive polymer in the
initial conductive polymer/host polymer blends as
measured in Example 5.

15   Fig. 9 provides Fowler-Nordheim plots derived in
Example 6 for polymer grid-containing single carrier
("hole-only") devices with 5% and 25% conductive
polymer in the initial conductive polymer/host polymer
blends. Similar data obtained from diodes rather than
triodes without the polymer grid are shown for

20   comparison.

Fig. 10 shows light intensity of a light-emitting
polymer grid triode with PVK as the first active
electronic material and MEH-PPV as the second and third
active electronic materials. The data are compared with

25   results from devices with the polymer grid alone; i.e.
without the PVK layer. These data were generated in
Example 7.

Fig. 11 shows efficiency of a light-emitting
polymer grid triode with PVK as the first active

30   electronic material and MEH-PPV as the second and third
active electronic materials. The data are compared with
results from devices with the polymer grid alone; i.e.
without the PVK layer. These data were generated in
Example 7.

35   Fig. 12 is a graph comparing light intensity vs
applied voltage for light-emitting devices containing

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and not containing a polymer grid. These data were generated in Example 7.

Fig. 13 is a graph comparing light intensity vs applied voltage for polymer grid-containing devices with and without a polyaniline active electronic material. These data were generated in Example 8.

Fig. 14 is a graph comparing efficiency vs current for polymer grid-containing devices with and without a polyaniline active electronic material. Thee data were generated in Example 8.

Fig. 15 is a graph comparing light intensity vs applied voltage for light-emitting devices containing and not containing a polymer grid. These data were generated in Example 8.

Fig. 16 is a schematic, not-to-scale cross sectional view of a polymer grid triode described in Example 9.

Fig. 17 is a series of graphs of the polymer grid triode cathode (C) current vs voltage (I_{AC} vs V_{AC}) curves for the polymer grid triode of Fig. 14 at different voltages between the anode and the polymer grid electrode.

Fig. 18 is a pair of graphs showing the anode to cathode current (I_{AC} vs V_{AC}) is independent of the voltage between the polymer grid network when measured at a different position in the device of Fig. 14, a position not affected by the polymer grid.

Fig. 19 is a schematic, not-to-scale cross sectional view of a polymer grid triode described in Example 10.

Fig. 20 is a graph of polymer grid triode current-voltage characteristics showing anode (A) - cathode (C) current vs voltage (I_{AC} vs V_{AC}) curves for a polymer grid triode of Example 10 for different voltages between the anode and the polymer grid electrode.

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Fig. 21 shows the anode to cathode current (I_{AC} vs V_{AC}) for various voltages between the polymer grid and the ITO anode network in the device of Example 10.

Fig. 22 shows directly the anode-to-cathode current (I_{AC}) for the device of Example 10 as a function of the voltage between the network electrode and the anode.

Fig. 23 illustrates polymer grid triode current-voltage characteristics showing anode (A) - cathode (C) current vs voltage (I_{AC} vs V_{AC}) curves for a polymer grid triode of Example 11 for different voltages between the anode and the polymer grid electrode.

Fig. 24 directly presents the anode-to-cathode current (I_{AC}) as a function of the voltage between the network electrode and the anode in the device of Example 11.

Fig. 25 is a schematic, not-to-scale cross sectional view of a light-emitting polymer grid triode described in Example 12.   Figs. 26-28 are a series of graphs based on data gathered in Example 12.

Fig. 26 shows the anode (A) - cathode (C) current vs voltage (I_{AC} vs V_{AC}) curves for different voltages (V_G) between the cathode and the polymer grid electrode.

Fig. 27 shows the light emitted from the polymer grid triode as a function of the anode-to-cathode voltage (V_{AC}) for several different grid-anode bias voltages (V_G).

Fig. 28 shows the light emitted at constant V_{AC} (for V_{AC} = 2V, 5V, and 6V) as a function of V_G.

Fig. 29 is a schematic, not-to-scale cross sectional view of a light-emitting polymer grid triode described in Example 13.

Fig. 30 is a series of graphs based on data gathered in Example 13 which shows the anode (A) -

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cathode (C) current vs voltage (I_{AC} vs V_{AC}) curves for different voltages (V_G) between the anode and the polymer grid electrode in the light-emitting triode of Fig. 27.

5   Fig. 31 is a series of graphs based on data gathered in Example 14 which shows the anode (A) - cathode (C) current vs voltage (I_{AC} vs V_{AC}) curves for different voltages (V_G) between the anode and the polymer grid electrode in the polymer grid triode of

10   Example 14.

Fig. 32 is a series of graphs also based on data gathered in Example 14 which shows the anode (A) - cathode (C) current vs voltage (I_{AC} vs V_{AC}) curves for different voltages (V_G) between the anode and an

15   altered polymer grid electrode in which the host polymer has not been removed.

Fig. 33 is a graph showing a I_{AC} vs V_{AC} curve for the light-emitting polymer grid triode of Example 15.

Fig. 34 is a graph that shows the light emitted

20   from the polymer grid triode of Example 15 as a function of the anode-to-cathode voltage (V_{AC}) for several different grid-anode bias voltages (V_G).

Fig. 35 is a pair of graphs based on data generated in Example 16. I_{AC} vs V_{AC} curves are plotted

25   at $V_G=0$ (zero grid current) and at $V_G=0.07V$ with $I_G=0.1$ mA to show the effect of the grid current on I_{AC} at various V_{AC} bias levels.

Fig. 36 is a series of graphs showing: I_{AC} vs V_{AC} characteristics of an Al/MEH-PPV/PANI-CSA/MEH-PPV/Ca

30   polymer grid TFT for various grid voltages, V_G, applied between the PANI-CSA network grid and the Al cathode.

Fig. 37 is a series of graphs of I vs V curves (on semilog scale) for the Al/MEH-PPV/PANI-CSA half of the device and for the PANI-CSA/MEH-PPV/Ca half of the

35   device show that both exhibit the expected diode behavior.

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Open circles: PANI-CSA/MEH-PPV/Al

Closed circles: PANI-CSA/MEH-PPV/Ca

Fig. 38 is a series of graphs of I_{AC} vs V_{AC} characteristics of a Al/MEH-PPV/PANI/MEH-PPV/CA polymer grid triode plotted on a semilog scale; for successively higher values of $|V_G|$, the steep onset of I_{AC} (which defines the flat band condition) moves proportionally to higher values of $|V_{AC}|$.

Fig. 39 is a graph of the current gain, $G = \Delta I_{AC}$ /ΔI_G, of an Al/MEH-PPV/PANI/MEH-PPV/Ca device, where ΔI_G is the change in grid current in the anode-to-cathode circuit.

Fig. 40 is a schematic of the test circuit used to gather the data shown in Fig. 39.

Best Mode for Carrying Out the Invention

The structure of a representative polymer grid triode is set forth in Fig. 1. The structure shown there includes an optional substrate 10 with the typical elements of the triode labeled as (1) through (5). A first electrode (1) is in contact with a first active electronic material (2), the top of which is in contact with the grid electrode (3) comprising a conducting polymer and an optional second active electronic material (3'). The top of the grid electrode is in contact with a third active electronic material (4), which is in contact with a second electrode (5).

The first and second electrodes, (1) and (5), in either order, are analogous to the anode and/or cathode of the vacuum tube triode; the polymer grid electrode (3) is analogous to the grid electrode of the vacuum tube triode. The first, second and third active materials ((2), (3'), and (4) transport electronic charge carriers. The transport is controlled and affected by the polymer grid electrode (3). The active electronic materials, (2), (3') and (4), which transport electronic charge carriers from (1) to (5)

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are conductors with various levels of electrical
conductivity, one or more of which can be, for example,
semiconductor materials; the active electronic
materials, (2), (3') and (4), within the polymer grid
triode can be the same, or they can be different. In
addition, while it is the case with the polymer grid
triodes that active electronic material is present
between the first and second electrodes, it is not
required that active material always be present in all
three locations. Thus, in some embodiments the polymer
grid triodes may omit one or two of the active
materials (2), (3') and (4).

In one embodiment of the polymer grid triode, the
grid electrode (3) is a high surface area porous but
electrically substantially continuous network made up
of conducting polymer. The high surface area and
porosity is reflected in a surface area of at least
about 10 cm^2/gram, such as at least 25 and often at
least 50 or even 100 cm^2/gram and porosity values of at
least about 1%, especially at least about 5%, and often
at least about 25%. Semiconducting material (3')
fills, or partially fills, the void spaces within the
high surface area porous network. The filled network is
deposited on the first active electronic material (2)
in contact with the first electrode (1) on a substrate.
The top surface of the filled network grid electrode,
(3) and (3'), is in contact with (4), which is in
contact with the second electrode. Since there is a
continuous path of conducting materials between the
electrodes (1) and (5) and through the polymer network
grid electrode (3), this configuration, shown in Fig.
1, is that of a polymer grid triode. Also, since the
distance between the first and second electrodes (1)
and (5) is set by the thickness of the layers in a
vertical configuration, sub-micron dimensions are

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easily achieved by fabricating (1) through (5) in the
form of thin films.

The materials chosen as conductive polymers for
forming the polymer grid and as active electronic
materials for elements (2), (3') and (4) play a direct
role in determining the characteristics and performance
of the triodes. For example, if one or more of the
active electronic materials are luminescent, light-
emitting polymer grid triodes can be achieved.

Polymer grid triodes can be either single-carrier
or two-carrier devices. For single-carrier devices,
carriers are injected at one electrode and withdrawn at
the second electrode; for example, holes are injected
into otherwise filled energy states of the
semiconducting material at the anode and withdrawn at
the cathode. For two-carrier polymer grid triodes,
holes are injected into otherwise filled energy states
of the semiconducting material at the anode, and
electrons are injected into otherwise empty energy
states at higher energy at the second electrode. For a
description and analysis of one-carrier and two-carrier
injection, see I.D. Parker, J.Appl. Phys., 75, 1656
(1994).

Generally, therefore, polymer grid triodes
comprise an anode and a cathode. The anode serves as a
hole injecting and/or electron withdrawing contact;
typically, a conducting material with relatively high
work function (relatively high ionization potential) is
used. The cathode serves as an electron injecting
and/or hole withdrawing contact; for example, a
relatively low work function metal (Ca, Al, or the
like) in the case of two-carrier devices, or metals
such as copper or silver for the case of
single-carrier, hole-only devices.

Single-carrier devices are useful and indeed often
preferable for polymer grid triodes, for in this case,

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one can use stable metals such as, for example, copper
or silver as the cathode (and hole withdrawing)
material.

    In the case of two-carrier light-emitting triodes,
5   one of the two electrodes (typically the anode) is at
least semi-transparent so as to enable the light to
exit from the device. Examples of suitable transparent
electrodes are indium/tin-oxide (ITO) and polyaniline
(PANI) in the conducting, protonated emeraldine salt
10   form. In two-carrier devices, the cathode is typically
a relatively low work function conducting material. Any
low work function (low ionization potential) conducting
material can be used as the electron injecting contact;
for example a conventional metal, a metal alloy or an
15   electropositive conducting polymer such as, for
example, n-type doped polyquinoline. The
electropositive and electronegative character of the
electrodes can be defined with respect to the
semiconducting material within the polymer grid triode
20   by standard electrochemical means.

    ITO has been the most commonly used transparent
electrode for EL devices. On the other hand, PANI, in
the emeraldine salt form prepared according to U.S.
Patent No. 5,232,631, and in Applied Physics Letters,
25   60, 2711 (1992), has a higher work function than ITO,
and therefore provides better hole injection into the
polymer active layer. However, the surface resistance
of a very thin PANI film often is too high for some
applications. In order to avoid significant voltage
30   drop in the electrode, it is desirable to decrease the
surface resistance of the anode to less than about 100
ohms/square. Although this can be achieved using a
thicker layer (>2500Å) of PANI, the transmittance of
such a PANI electrode is less than 70%, which would
35   lead to more than a 30% loss in external quantum
efficiency. United States patent application Serial No.

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Applied Physics Letters, <u>64</u>, 1245 (1994) disclosed that
when an ITO electrode is coated with an ultrathin layer
(typically <1000Å) of PANI, the bilayer electrode thus
obtained has a minimum transmittance (~ 500nm) at

5   around 90%, a work function similar to that of PANI
alone and a surface resistance below that of ITO. The
bilayer PANI/ITO electrode offers special advantages
for use in EL devices with improved efficiency and
lower operating voltages.

10   The polymer grid electrode (3):

The polymer grid electrode (3) can be fabricated
from a network comprising a conducting polymer.

Earlier work demonstrated that polyaniline, PANI,
self-assembles into a conducting network morphology in

15   blends with poly(methylmethacrylate) (C.Y. Yang, Y.
Cao, P. Smith and A.J. Heeger, Synth. Met. <u>53</u>, 293
(1993)). Near the percolation threshold, the network
is fractal with a very high surface area at the
PANI:host interface (Reghu Menon, C.O.Yoon, C.Y. Yang,

20   D. Moses and A.J. Heeger, Macromolecules, <u>26</u>, 7245
(1994)). The connected pathways in the PANI-CSA network
cause such blends to exhibit electrical conductivity
with values in excess of 1 S/cm at volume fractions of
only a few per cent (w/w) PANI-CSA where CSA denotes

25   camphor sulfonic acid. After selectively etching out
the host polymer, the remaining conducting PANI-CSA
network is rough and porous, and has a high surface
area. This high surface area, porous network can be
used for the polymer grid electrode (3). In this way,

30   the contact area between the PANI-CSA and the active
material (3') which fills the porous network can be
increased dramatically. When the network is an
equipotential with respect to either the first or
second electrode (see Fig. 1), the surface roughness,

35   with pointed and sharp fibrillar features, causes the
electric field lines to be non-uniform, thereby

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enhancing the local electric field in regions near the network.

The polyaniline useful in this invention may vary widely and is not critical. Useful conductive polyanilines include the homopolymer, derivatives and blends with bulk polymers, which herein are collectively referred to as PANI. Examples of PANI are those disclosed in U.S. Patent 5,232,631, which is incorporated by reference herein. Preferred PANI has a bulk conductivity of at least 10^{-3} S/cm. More preferred PANI has a bulk conductivity of at least 10^{-1} S/cm. Still more preferred PANI has a bulk conductivity of at least 1 S/cm. Most preferred PANI has a bulk conductivity of at least 100 S/cm.

Other network-forming conducting materials can be used in place of PANI. For example, conductive forms of polypyrrole can be polymerized within a porous matrix polymer (A. Mohammadi, I. Lundstrom, O. Inganas and W.R. Salaneck, Polymer, 31, 395 (1990)).

The method by which the porous conducting network is formed is not critical; the critical feature is that the resulting network be open and porous. Although any network forming material can be used, the ability to create the network spontaneously through self-assembly, as is the case for PANI, offers a special advantage to the fabrication of polymer grid triodes.

In one embodiment for forming the open network with access to the voids within the porous network, the metallic emeraldine salt form of PANI is prepared by protonation with functionalized sulfonic acids (e.g. CSA), yielding a conducting PANI-complex which is soluble in common organic solvents (Y. Cao, G. M. Tracy, P. Smith and A.J. Heeger, Appl. Phys. Lett. 60, 2711(1992). Y. Cao, P. Smith and A.J. Heeger, Synth. Met. 48, 91 (1992)). PANI-CSA solutions (2%, w/w) were prepared using meta-cresol as the solvent. A highly

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soluble low molecular weight (M$_w$ < 10,000) polyester resin, PES, was used; the PES was separately dissolved in meta-cresol at a concentration of 20% w/w. Different concentrations of PANI:PES blends were prepared by mixing the PANI and PES solutions at different ratios; concentrations of PANI:PES were prepared at 5%, 10%, 25%, 40% and 100% in order to optimize the effects of high surface area and surface roughness. The PANI:PES blends were spin-cast onto glass substrates (half-coated with ITO) and subsequently dried in air at 50°C for 12 hours. Subsequently, the PES was removed from the blend by exposing the PANI:PES blend thin film to a solvent which dissolved only the PES, leaving the conducting PANI network open, porous, and intact.

The Polymer Grid Electrode (3) Filled with Active Electronic Material (3'):

A wide variety of semiconducting and/or luminescent materials well known in the art can be used to fill, or partially fill, the open void spaces within the porous network. These include inorganic semiconductors such as silicon and especially amorphous silicon (deposited for example by chemical vapor deposition, CVD), semiconducting organic polymers, both conjugated and nonconjugated, and blends of conjugated polymers in host polymers, small molecule organic semiconductors and the like.

Examples of semiconducting conjugated polymers include but are not limited to poly(phenylenevinylene), PPV, and soluble derivatives of PPV, such as MEH-PPV (US Patent No. 5,189,136) and BCHA-PPV (US. Patent Application 07/626463), PPPV (C.Zhang et al, in Synth.Met., 62, 35, (1994) and references therein) and the like, the soluble derivatives of polythiophene, for example the poly(3-alkylthiophenes) (C. Zhang et al, J. Appl.Phys. 73, 5177, (1993)) and other semiconducting

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conjugated polymers, some of which exhibit
photoluminescence; and blends of such semiconducting
and/or luminescent conjugated polymers in
hole-transporting or electron transporting polymers
5   (C.Zhang et al, in Synth.Met., 62, 35, (1994)).

Small molecule semiconducting and/or luminescent
organic materials can be used, such as those disclosed
in the following: (C.W. Tang, S.A. Van Syke, Appl.
Phys. Lett. 51, 913 (1987); C.W. Tang, S.A. Van Syke
10   and C.H. Chen, J. Appl. Phys. 65, 3610 (1989); C.W.
Tang, S.A. Van Syke, U.S. Patent No. 4,769,292; C.
Adachi, S.Tokito, T.Tetsui and S. Saito, Appl. Phys.
Lett., 55, 1489 (1989); C. Adachi, S.Tokito, T.Tetsui
and S. Saito, Appl. Phys. Lett., 56, 799 (1989); M.
15   Nohara, M. Hasegawa, C. Hosohawa, H. Tokailin, T.
Kusomoto, Chem. Lett. 189 (1990)). Examples include but
are not limited to the following:

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RECTIFIED SHEET (RULE 91)
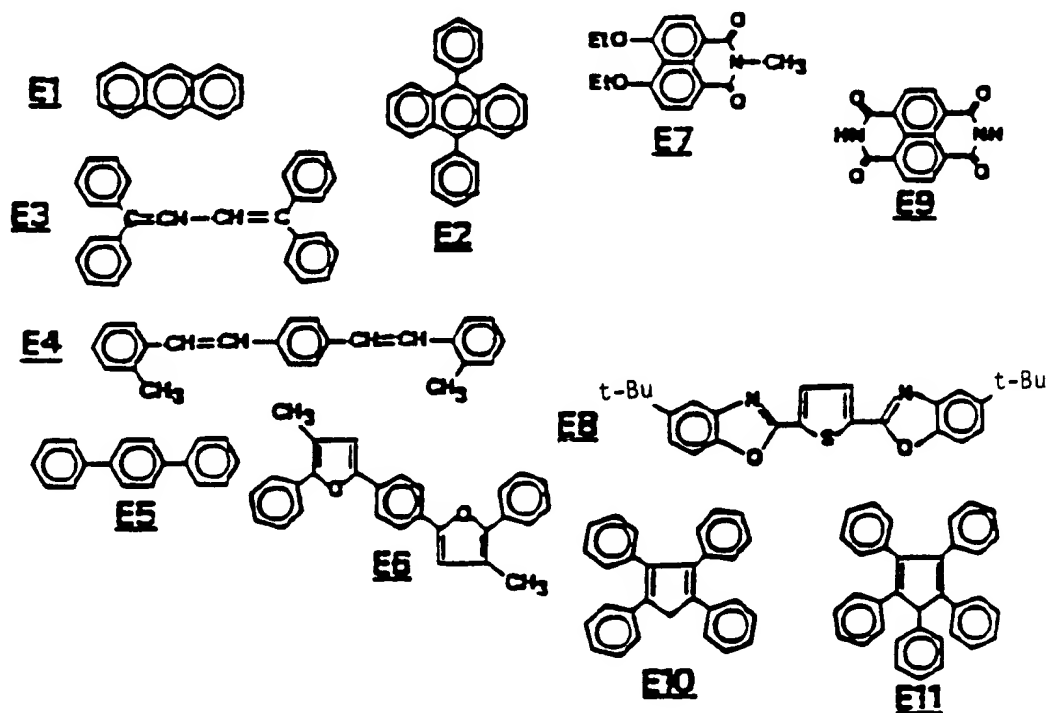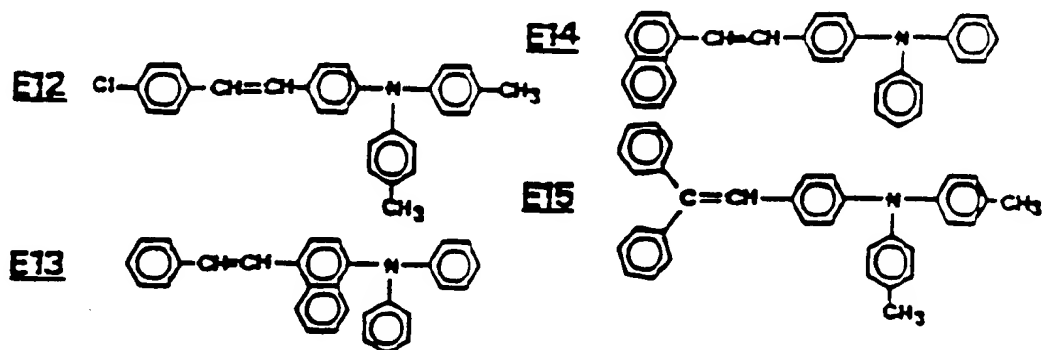
In the case of small molecule semiconducting and luminescent organic materials, the material is sublimed (vacuum evaporation) and deposited directly into the open voids of the pre-formed porous network. Oligomers of thiophene, for example, comprising four, five or six thiophene rings, are known in the prior art and have been sublimed to form thin films for use in FETs (F. Garnier, G. Horowitz, X. Peng, and D. Fichou, Adv. Mater. 2, 592 (1990)).

Inorganic semiconductors can be used, a requirement being that such inorganic semiconductors be deposited by a sufficiently low temperature process that the network is not adversely affected. For example, CVD methods can be used to deposit inorganic semiconducting material into the open voids within the porous network.

In the case of semiconducting polymer materials, the active semiconducting (and luminescent, when appropriate) material may be cast from solution into the open void spaces within the porous network. In this case, the semiconducting material must be in solution in a solvent which does not dissolve the conducting network material. Alternatively, the active electronic material might be vapor deposited into the voids.

Typical film thicknesses for the network grid electrode filled with semiconductive material range

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from a few hundred Angstrom units to a few thousand
Angstrom units (1 Angstrom unit = 10^{-8} cm). Although the
active film thicknesses are not critical, polymer grid
triode performance can typically be improved by using
5   thinner networks.

In one embodiment, MEH-PPV was spin-cast at 1000
rpm from solution in xylene directly onto the thin film
of the PANI:PES blend. Since xylene is an excellent
solvent for PES, the PES in the PANI:PES blend was
10   etched out by the xylene and subsequently carried away
by the excess MEH-PPV solution during the spin-casting
process. Hence, in a single step, MEH-PPV replaced PES
to fill the voids in the porous structure within the
PANI:PES network. This concept can be readily
15   generalized to other soluble semiconducting materials.

The various elements of the devices of the present
invention can be fabricated by any of the techniques
well known in the art, such as solution casting,
sputtering, evaporation, chemical vapor deposition,
20   precursor polymer processing, melt-processing, and the
like, or any combination thereof.

Built-in Potentials:

Because the anode, the cathode, and the polymer
grid electrode are typically fabricated from different
25   materials, there are built-in potentials at zero bias;
i.e. at zero voltage between the anode and the cathode,
at zero voltage between the polymer grid electrode and
the anode, and at zero voltage between the polymer grid
electrode and the cathode.
30   The design of polymer grid triodes for specific
circuit applications should take into account the use
of particular conducting materials for the electrodes.
The electrode materials should have work functions
which optimize the electrode's characteristics needed
35   for that application. For example, a polymer grid

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triode with gold as the anode and cathode and a polymer grid with PANI as the network polymer has built in potentials analogous to those found in a PNP transistor.

Similarly, for example, the conducting form of PANI is more electronegative than ITO. Thus, for example, if the anode is ITO and the polymer grid electrode comprises PANI, there will be a built-in potential equal to the difference in work functions between PANI and ITO. Ca has a low work function. Thus, for example, if Ca is used as the cathode material and the polymer grid electrode comprises PANI, there will be a built-in potential between the cathode and the polymer grid electrode equal to the difference in work functions between Ca and PANI. These built-in potentials can be estimated from knowledge of the relative electrochemical potentials, or alternately from knowledge of the relative work function of the materials which comprise the cathode, the anode, and the network electrode.

Since in general the external voltage between any two of the three electrodes is applied in addition to the built-in potential between that pair of electrodes, the built-in potentials affect the response of the polymer grid triode to external voltages. The design of polymer grid triodes for specific circuit applications should utilize specific conducting materials for the electrodes, said materials having work functions which optimize the electrical characteristics for that application. For example, a polymer grid triode, with gold (Au) as the anode and cathode and with the polymer grid comprising PANI in the conducting form, has built-in potentials analogous to a pnp-transistor. Similarly, a polymer grid triode with aluminum, as the anode and cathode and with a polymer grid comprising polyaniline has built in

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potentials analogous to an npn transistor. Analyses of
the current vs voltage and/or light output vs voltage
and/or light output vs current of polymer grid triodes
are useful for planning the utilization of such polymer
grid triodes in circuit applications. When carrying out
such analyses, it is useful to include the built-in
potentials.

The electronic structure of the polymer grid
triode is analogous to that of npn or pnp transistors;
in each case the device can be viewed as constructed
from two coupled diodes, connected back-to-back.
Polymer grid triodes utilize semiconducting
polymer/electrode systems which are known to form high
quality diodes. Important examples include PANI-
CSA/MEH-PPV/Ca and PANI-CSA/P3OT/Au, both of which are
diodes with high rectification ratio.

In the PANI-CSA/MEH-PPV/Ca diode, Ca is the
cathode, and PANI is the anode and in the PANI-CSA/MEH-
PPV/Al diode, AL is the cathode, and PANI is the anode;
whereas in the PANI-CSA/P3OT/Au diode, PANI is the
cathode, and Au is the anode.

The electronic structure of the Al/MEH-PPV/PANI-
CSA/MEH-PPV/Ca polymer grid triode is shown
schematically in Fig 2. As shown in Fig 2A, under zero
bias conditions, there is a common chemical potential.
As a result of the different work functions of the Al,
PANI-CSA and Ca layers, the built-in potential is
analogous to that of a npn transistor. Fig 2B depicts
the flat-band condition where current just begins to
flow. As depicted in Fig 2C, at still higher anode-to-
cathode voltages (V_{AC}), the device is turned-on;
electrons are injected into the π*- band of MEH-PPV at
the Al electrode. The electric field in the
semiconductor forces the injected electrons toward the
polymer grid. If the polymer network is of
sufficiently low density, some fraction of the injected

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carriers will continue to still lower energy and be
withdrawn at the Ca anode. Under these conditions,
current (I_{AC}) will flow in the external anode-to-cathode
circuit. I_{AC} can be controlled by varying the grid
5   bias. With reverse bias on the input diode, I_{AC} will be
limited by the reversed bias current, as shown in Fig
2. If the rectification ratio is high, I_{AC} will be cut-
off by the bias voltage applied to the polymer grid.
This condition is depicted in Fig 2D as shown in the
10   Examples, this is indeed the case.

It should be noted that the four bias conditions
shown in Fig 2 are each drawn with the Ca electrode
grounded (the anode) and the Al electrode as the
cathode. These could be interchanged; i.d. the Ca
15   electrode used as the cathode and the grounded Al
electrode used as the anode.

The importance of the polymer network grid is
evident by the structures shown in Fig 2. Since PANI-
CSA is an excellent "hole injector" for MEH-PPV, (Y.
20   Yang and A.J. Heeger, Appl. Phys. Lett., 64, 1245
(1994). PANI-CSA is also an excellent "electron
extractor" from MEH-PPV. Thus if one were to fabricate
the Al/MEH-PPV/PANI-CSA/MEH-PPV/Ca device with a solid
film of PANI, there could be no true I_{AC}. Under forward
25   bias conditions shown in Fig 2, any electrons injected
at the Ca electrode would be extracted at the PANI
electrode. The device would be equivalent to two
uncoupled diodes connected back-to-back with no
possibility of gain. In this sense, the analogy of the
30   polymer network grid in the polymer grid triode with
the grid in the vacuum tube triode is genuine.

The electronic structure of the Au/P3OT/PANI-
CSA/P3OT/Au polymer grid triode is shown in Fig 3. As
shown in Fig 3A again, under zero bias conditions there
35   is a common chemical potential. In this case, since Au
is more electronegative than PANI-CSA, the built-in

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potential is analogous to that of an pnp transistor.
Fig 2B also shows the same device in the flat-band
condition where I_{AC} just begins to flow. As shown in
Fig 3C at still higher voltages, holes are injected
into the π-band of P3OT at the Au anode, and the
internal electrical field forces the injected holes
toward the polymer grid. If the polymer network is of
sufficiently low density, some fraction of the injected
holes will continue to still lower energy and be
withdrawn at the Au cathode. Under these conditions,
I_{AC} will flow in the external anode-to-cathode circuit.
I_{AC} can be controlled by varying the grid bias. With
reverse bias on the input diode, I_{AC} will be limited by
the reversed bias current, as shown in the Fig 3D.
Once again, if one were to fabricate the Au/P3OT/PANI-
CSA/P3OT/Au device with a solid film of PANI-CSA, there
could be no true I_{AC}; under the conditions shown in
Fig. 2, any holes injected at the Au anode would be
extracted at the PANI electrode. The device would
again be nothing more than two diodes connected back-
to-back with no possibility of gain.

The electronic structures shown in Figs 2 and 3
are drawn assuming each anode/polymer/cathode tri-layer
is a tunnel diode, as described in detail by Parker
(I.D. Parker, J. Appl. Phys., 75, 1656 (1994)).
Similar drawings can be made for anode/polymer/cathode
Schottky-like diodes, as would be appropriate when the
depletion length in the polymer semiconductor layer is
much less than the layer thickness (S.M. Sze, Physics
of Semiconductor Devices (Wiley, New York, 1981)).

Control of the Balance of Electron and Hole
Currents by Polymer Grid Electrodes

In a two-carrier polymer grid triode three
terminal device, when the polymer grid electrode is
biased negative with respect to the anode, electron

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transport is inhibited. The hole current can be similarly controlled by a polymer grid.

Thus, the ability to separately control and balance the electron and hole currents can be designed into such devices by including two independent network grids, separated by a semiconductor layer, that can be separately biased with respect to the anode and the cathode, respectively.

The following general methods and specific examples are presented merely to illustrate the invention and are not to be construed as limitations thereon.

EXAMPLES

Example 1

A polymer grid triode as shown in Fig. 1 was prepared but without the cathode layer (5). The metallic emeraldine salt form of PANI was prepared by protonation with functionalized sulfonic acids (for example, CSA or dodecylbenzenesulfonic acid, DBSA), yielding a conducting PANI-complex soluble in common organic solvents. In this Example, PANI-CSA solutions (2%, w/w) were prepared using meta-cresol as the solvent. A highly soluble low molecular weight ($M_w <$ 10,000) polyester resin (PES) was separately dissolved in meta-cresol at a concentration of 20% w/w and used to make the PANI:PES blends. Different concentrations (w/w) of PANI:PES blends were prepared by mixing the PANI and PES solutions at different ratios. In this Example, concentrations of PANI:PES were prepared at 5%, 10%, 25%, 40% and 100%. The PANI:PES blends were spin-cast onto glass substrates (half-coated with ITO) and subsequently dried in air at 50°C for 12 hours. The thickness of the different PANI:PES layers was held constant at ~1200Å. MEH-PPV was then spin-cast at 1000

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rpm from solution in xylene (8 mg/ml concentration).
Since xylene is also an excellent solvent for PES, the
PES in the PANI:PES blend was etched out by the xylene
and subsequently carried away by the excess MEH-PPV

5   solution during the spin-casting process. Hence,
MEH-PPV replaced PES in the porous structure within the
PANI:(PES) network, thereby increasing the interface
area between MEH-PPV and the PANI-CSA electrode; the
bracket, ( ), designating that the PES had been

10   removed.

Curve A of Fig. 4 shows the absorption spectrum of
a PANI:PES blend at a concentration of 5% (w/w) PANI.
The absorption peak characteristic of PES is clearly
seen at 290nm. The absorption spectrum of the

15   PANI:(PES) layer over-coated with MEH-PPV is also shown
as curve B in Fig. 1. The PES peak has disappeared
after the spin-casting step during which the MEH-PPV
layer was deposited (the MEH-PPV absorption is clearly
seen); a clear indication that the PES was removed by

20   the xylene of the MEH-PPV polymer solution and replaced
by MEH-PPV within the porous network. Absorption
measurements of PANI:PES blends with other
concentrations of PANI showed the same indications of
PES removal (and replacement by MEH-PPV) after

25   over-coating with MEH-PPV.

This Example demonstrates that the conducting
network can be formed and that said network can be
filled with semiconducting and/or luminescent material.
The filled conducting network can be used to fabricate

30   the polymer grid (3) filled with the active electronic
material (3'), as shown in Fig. 1.

Example 2:

The surface of the MEH-PPV film above the
PANI-network layer is very rough for PANI:PES blends at

35   concentrations near the percolation threshold (e.g. 1%

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and 5%). Using a Dektak profilometer, the length scale
of the surface roughness of the network filled with
MEH-PPV which initially contained 5% PANI was measured;
the peak to valley variations were ~300-400Å. Light
scattering by the residual PANI-CSA network at these
concentrations was quite strong, an additional
indication of surface roughness. The surface roughness
of the MEH-PPV film is diminished when 10% PANI:PES
blends were used; at concentrations of PANI-CSA in
excess of 25%, the PANI-CSA anode appeared smooth to
the Dektak probe.

This example demonstrates the existence of surface
roughness associated with the conducting network used
for fabricating the polymer grid electrode (3) of Fig.
1.

Example 3:

The electrical conductivity of the PANI:PES blends
was monitored by measurements using the standard two
probe technique. Fig. 3 shows the conductivity of the
PANI:PES blends as a function of the PANI weight
fraction. Conductivities of order 1 S/cm were obtained
in blends containing as low as 1% PANI-CSA. The
conductivity of the network showed a steep initial
increase, leveling off at about 25% PANI-CSA at
conductivities close to 200 S/cm, similar to results
reported earlier for PANI-CSA:PMMA blends (C.Y. Yang,
Y. Cao, P. Smith and A.J. Heeger, Synth. Met. 53, 293
(1993)).

The resistance of the PANI:PES film was measured
both before and after the MEH-PPV spin-casting process
to ensure that the PANI network remained intact. The
data in Table 1 show the PANI network resistance before
and after removal of the PES during spin-casting the
MEH-PPV. The resistance values of the 1% and 5% blends
actually *decreased* by 10-20% after spin-casting the

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MEH-PPV layer, while the 10%, 25% and 40% samples showed no significant changes. Thus, the PANI network remains after spin-casting the active luminescent polymer layer. Most likely, the decrease in resistance observed upon removal of the PES from the dilute PANI:PES blends was due to the partial collapse of the tenuous initial PANI-CSA network, resulting in increased contact between the conducting polymer (PANI) fibrils.

This Example demonstrates that the conducting PANI network is robust and remained intact during and after subsequent processing steps. Thus, the PANI network can be used in the fabrication of the polymer grid electrode (3) filled with active electronic material (3').

TABLE 1:
Resistance Values of PANI:PES Blends
Before and After Removal of the PES

% PANI	Resistance before removal of the PES (Ω)	Resistance after removal of the PES (Ω)	Change
1	70.4KΩ	53.8KΩ	-24%
5	6.1KΩ	5.1KΩ	-16%
10	800Ω	810Ω	+1.3%
25	650Ω	640Ω	-0.6%
40	410Ω	440Ω	+6%

Example 4:

Fig. 4 shows the current vs voltage (I_{AC} vs V_{AC}) characteristics between the first and second electrodes (anode, A, and cathode, C) of ITO/PANI-network/MEH-PPV/Ca light-emitting structures with different initial concentrations of PANI:PES in

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the network electrodes: 10% PANI:(PES) (closed
circles), 25% PANI:(PES)(open circles), and 40%
PANI:(PES) (diamonds); the bracket, (   ), denotes that
the PES had been removed from the PANI network. In all

5   three cases, because of the asymmetric cathode (low
work function) and anode (higher work function), the I_{AC}
vs V_{AC} curves were rectifying; in each case the
rectification ratio was greater than 1000 (ratio of
forward to reverse current at ± a specific applied

10   voltage).

        Similar devices using pure PANI/ITO (i.e. 100%
PANI) as the electrode were also fabricated for
comparison. Charge carrier injection into the MEH-PPV
was enhanced dramatically by using the PANI-network

15   electrode, resulting in significantly lower device
operating voltages (closed triangles in Fig 6). The
smaller concentrations of PANI in the initial PANI:PES
blends provided higher surface area and hence better
charge injection and progressively lower device

20   operating voltages.

        This Example demonstrates enhanced carrier
injection with polymer network grids over that in
similar devices without the polymer network grids.

Example 5:

25   Light emission from the devices fabricated with
the light-emitting polymer grid was measured using the
devices for which the I_{AC} vs V_{AC} curves were measured in
Example 4. In all cases, the electroluminescent
emission was proportional to the current. Fig. 7 shows

30   the external quantum efficiency (QE) of these devices;
the QE was maximized at a concentration of PANI in the
initial PANI:PES blend of approximately 25%.

        The PANI-network electrode dramatically increases
the brightness of the electroluminescent emission. Fig.

35   8 shows the brightness at 4 volts forward bias as a

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function of the concentration of PANI-CSA in the initial PANI:PES blends. The data in Fig. 8 were obtained from a series of devices all with the same thickness of MEH-PPV (1300 Å). For 10% PANI in the

5   initial blends, the brightness was approximately 160 cds/m^2, an increase by nearly two orders of magnitude over that obtained from the simple PANI/ITO bilayer.

This Example demonstrates that light emission is enhanced by the polymer grid; the electroluminescent

10   emission turns on at a significantly lower voltage with brightness that is significantly enhanced over emission from devices without the polymer grid electrode.

Example 6:

The strong local electric field caused by the

15   roughness of the PANI-CSA electrode serves to further enhance charge injection. Charge is injected from the electrodes into the π (for holes) and $\pi*$ (for electrons) bands of MEH-PPV via tunneling (I. D. Parker, J. App. Phys, 75, 1656 (1994)). Fowler-Nordheim

20   field-emission tunneling theory predicts (R. H. Fowler and L. Nordheim, Proc. Roy. Soc. (London), 119A, 173 (1928)):

$$I \propto F^2 \exp\left(\frac{-\kappa}{F}\right) \qquad\qquad (1)$$

where I is the current, F is the electric-field strength, and k is a parameter that depends on the

25   shape of the barrier at the metal-polymer contact. Assuming that the injected charge tunnels through a triangular barrier at the interface , the constant k in

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Eqn 1 is given by (S. M. Sze, *Physics of Semiconductor Devices* (Wiley, New York, 1981)).

$$\kappa = \frac{8\pi\sqrt{2m^*}\varphi^{3}/_{2}}{3qh} \qquad (2)$$

In Eqn 2, ϕ is the barrier height, and m^* is the effective mass of holes in the semiconducting polymer. Eqn 2 assumes that the electric field is constant across the device and that the effective mass equals the free electron mass. Since the barrier height associated with the PANI-CSA/MEH-PPV interface was measured in parallel experiments using dense PANI films as electrodes, Eqns 1 and 2 can be used to infer the enhancement in the local field, F_{loc}, by assuming that κ_0 is determined by the intrinsic barrier height (ϕ_0) which is characteristic of the PANI-CSA/MEH-PPV interface. A Fowler-Nordheim plot can therefore be used to directly estimate the local field enhancement.

    To measure the apparent barrier height at the roughened PANI/MEH-PPV interface, hole-only devices were fabricated using copper (Cu) as the cathode material. Fig. 9 shows a plot of $\ln(I/F^2)$ vs. $1/F$ for a PANI:PES(25%)/MEH-PPV/Cu device, a PANI:PES(5%)/MEH-PPV/Cu device, and a PANI(no PES)/MEH-PPV/Cu device, all fabricated with a 1300Å MEH-PPV layer. Since the plot assumed a uniform electric field strength across the MEH-PPV, the resulting estimate of the electric field was an average; the actual local field was even larger near sharp features in the PANI network electrode.

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The barrier heights for the PANI network
electrodes were calculated using Eqns, 1 and 2 . As
shown in Fig 9, the barrier height for PANI was 0.1e V,
for 25% PANI [PES] was 0.04eV and for 5% PANI [PES] was

5   0.023 eV). The 0.1eV barrier height characteristic of
the PANI/MEH-PPV interface was apparently lowered by
forming the roughened PANI high surface area electrode;
e.g. for the 5% PANI:PES blend network, the apparent
barrier height was lowered by a factor of five. Using

10   Eqn 1 and 2 and the data for the apparent barrier
height as indicated in Fig. 9, the data indicated that
the average local field was enhanced by approximately
an order of magnitude.

This Example demonstrates that the enhanced local

15   electric field is a feature of the irregular rough
surface of the self-assembled PANI-CSA network
electrode.

Example 7:

A polymer grid light-emitting triode was

20   fabricated in the configuration shown in Fig. 1 with a
solid thin film of PVK as the first active electronic
material (2) and a PANI network electrode (3) filled
with MEH-PPV (3') as the polymer grid electrode. The
initial PANI:PES blend contained 5% PANI. The MEH-PPV

25   was filled into the network and the PES removed in a
single step. The MEH-PPV extended beyond the PANI
network to form the third active electronic material,
(4) in Fig. 1. ITO was used as the anode (for hole
injection) and Calcium was used as the cathode (for

30   electron injection).The results are shown in Fig.s 10-
12.

Using the polymer grid light-emitting triode
configuration with PVK as the first active electronic
material (2) yielded comparable light intensity (closed

35   circles Fig. 10) and higher efficiency (Fig. 11) than

35

with PANI network alone (open circles in Figs) and much
improved performance over use of ITO alone as the hole
injecting electrode in a diode configuration. Fig. 12
shows that the polymer grid light-emitting triode

5   (closed circles) had a turn-on voltage much below that
of the corresponding device (open circles) without the
filled network electrode. At 4 volts, the brightness
was in excess of 100 cds/m^2.

This Example demonstrates that the use of the

10   first active electronic material (in this case PVK),
(2) in the polymer grid triode configuration of Fig. 1,
serves to enhance the light emission from the
light-emitting polymer grid triode.

Example 8:

15   A polymer grid light-emitting triode was
fabricated in the configuration shown in Fig. 1 with a
solid thin film of PANI in the conducting, protonated
emeraldine salt form as the first active electronic
material (2) and a PANI network as the polymer grid

20   electrode (3) filled with MEH-PPV (3'). The initial
PANI:PES blend contained 5% PANI. The MEH-PPV was
filled into the network and the PES removed in a single
step (3'). The MEH-PPV extended beyond the PANI network
to form the third active electronic material (4) on

25   Fig. 1. ITO was used as the anode (for hole injection)
and calcium was used as the cathode (for electron
injection). The results are shown in Fig.s 13-15.

Using the polymer grid light-emitting triode
configuration with PANI as the first active electronic

30   material (2) (closed circles) yielded higher light
intensity (Fig. 13) and higher efficiency (Fig. 14)
than with PANI network alone (open circles) and much
improved performance over use of ITO alone as the hole
injecting electrode in a diode configuration. Fig 15

35   shows that the polymer grid light-emitting triode

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(closed circles) has a brightness significantly greater
than that of the corresponding device without the
filled network electrode (open circles).

This Example demonstrates that the use of the
first active electronic material (in this case PANI),
(2) in the polymer grid triode configuration of Fig. 1
serves to enhance the light emission from the
light-emitting polymer grid triode.

Example 9:

A polymer grid triode in the general configuration
of Fig. 1 and the more specific configuration of Fig.
16 was fabricated using the following materials for the
indicated layers and constituents:

Substrate (10): Glass

1st electrode (1): ITO

First active electronic material (2): 1000Å of
poly(phenylene vinylene), (PPV). The PPV-precursor
polymer PPV was cast directly onto the ITO electrode.
The precursor was converted to the semiconducting PPV
form using standard procedures well-known in the art
(heating to 220°C for a period of 2 hours).

Polymer grid electrode (3): 300Å of Polyaniline
filled with MEH-PPV (3'); the filled network was made
in a single step using an initial PANI:PES blend
containing 40% PANI. The filled network was fabricated
directly onto the PPV first active electronic material
layer (2) using the method described in Example 1. A
500Å gold contact (12) was applied to the grid.

Third active electronic material (4): MEH-PPV
(1400Å) was cast onto the filled network, (3) and (3').

2nd electrode (5A-5D): Gold (Au) metal was
deposited onto the third layer by vacuum evaporation.
The device was connected such that forward
anode-cathode bias corresponds to the anode (1)
positive with respect to the Au (5). The conducting

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polyaniline network polymer grid electrode was
electrically connected to an external battery circuit
such that a voltage was applied between the conducting
network and the electrode on the substrate (the anode).
5   The anode-cathode current vs voltage curves (I_{AC} vs V_{AC})
were determined using electrode 5C as cathode and are
shown for different voltages between the anode and the
polymer grid electrode in Fig. 17. In Fig 17, the top
(open circle) curve was obtained at a V_G of 0.45V, the
10   middle (closed circle) curve was obtained at a V_G of
0.0V and the lower (open circle) curve was obtained at
a V_G of -0.36V.

Since electron injection from the Au electrode was
negligible, this polymer grid triode was a
15   single-carrier device. The polymer grid triode
functioned as a three-terminal device; the
anode-cathode current was controlled by the voltage
between the anode and the polymer grid electrode.

Similar results were obtained with different
20   series resistance values in the polymer grid circuit
(1MΩ or 100KΩ). Thus, the three-terminal device can be
operated with the polymer grid biased at constant
voltage or with the polymer grid drawing significant
grid current.

25   Note that in the control experiment, the results
of which are illustrated in Fig. 18, (using second
electrode 5A, rather than second electrode 5C; see Fig.
16) the anode-to-cathode current was not affected by
the grid-to-anode voltage (open circles V_G = 2.2V,
30   closed circles V_G = 0.V.) This control experiment
directly verifies the importance of the polymer grid
electrode (the filled PANI network) in the operation as
a three-terminal device.

This Example demonstrates that the polymer grid
35   triode functioned as a three-terminal device; that the
anode-cathode current was controlled by the voltage

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between the anode and the polymer grid electrode, and that the role of the polymer grid electrode was critical to the operation, indicative of a three-terminal device.

5   Example 10:

A polymer grid triode in the general configuration of Fig. 1 and the more specific configuration of Fig. 19 was fabricated using the following materials for the indicated layers and constituents:

10   Substrate (10): Glass·

1st electrode (1): ITO

First active electronic material (2): Poly(vinyl carbazole), PVK. The PVK film (1500Å) was cast from cyclopentanone directly onto the ITO electrode.

15   Polymer grid electrode (3): Polyaniline filled with MEH-PPV (3'); the filled network was made in a single step using an initial PANI:PE blend containing 10% PANI. The filled network was fabricated directly onto the PVK layer (2) using the method described in

20   Example 1.

Third active electronic material (4): MEH-PPV cast onto the filled network, (3) and (3').

2nd electrode (5): Gold (Au) metal deposited onto the third layer by vacuum evaporation.

25   The device was connected such that forward anode-cathode bias corresponds to the anode (1) positive with respect to the Au electrode (5). The conducting polyaniline polymer grid electrode (3) was electrically connected to an external battery circuit

30   such that a voltage was applied between the polymer grid electrode and the first electrode (1). The anode-cathode current vs voltage (I_{AC} vs V_{AC}) curves are shown for different voltages applied between the anode and the network (3rd) electrode, V_G, in Fig. 20.

39

The polymer grid triode studied in this Example was a single carrier device, since electron injection from the Au electrode was negligible. The anode-to-cathode current is particularly sensitive to the network (grid) to anode voltage at V_{AC} between $\pm 10V$, where V_{AC} is the voltage applied between the anode and the cathode (positive voltage corresponds to the Au electrode negative with respect to the ITO electrode); see Fig. 21.

In Fig. 22, the current between anode and cathode (I_{AC}) is plotted as a function of the voltage between the polymer grid electrode (3) and the anode (1). Larger negative grid-to-anode voltages suppress the hole current.

Similar results were obtained with different series resistance values in the polymer grid circuit (1MΩ or 100KΩ). Thus, the three-terminal device can be operated with the polymer grid biased at constant voltage or with the polymer grid drawing significant grid current.

This Example demonstrates that the polymer grid triode functioned as a three-terminal device; the anode-cathode current was controlled by the voltage between the anode and the polymer grid electrode.

Example 11:

A polymer grid triode in the configuration of Fig. 1 was fabricated using the following materials for the indicated layers and constituents:

Substrate (10): Glass

1st electrode (1): ITO

First active electronic material (2): Poly(vinyl carbazole), PVK. The PVK film (1500Å) was cast from cyclopentanone directly onto the ITO electrode.

Polymer grid electrode (3): Polyaniline filled with MEH-PPV (3'); the filled network was made in a

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single step using an initial PANI:PMMA blend containing
5% PANI using toluene as the solvent. The filled
network was fabricated directly onto the PVK active
layer (2) using the method described in Example 1.

5   Third active electronic material (4): MEH-PPV was
cast onto the filled network (3) and (3').

2nd electrode (5): Gold (Au) metal was deposited
onto the third layer by vacuum evaporation.

The device was connected such that forward
10   anode-cathode bias corresponds to the anode (1)
positive with respect to the Au electrode (5). The
conducting polyaniline polymer grid electrode (3) was
electrically connected to an external battery circuit
such that a voltage was applied between the polymer
15   grid and (1). The anode-cathode current vs voltage
curves (I_{AC} vs V_{AC}) are shown for different voltages
between the anode and the polymer grid electrode in
Fig. 23.

The polymer grid triode studied in this Example
20   was a single carrier device, since electron injection
from the Au electrode was negligible. The
anode-to-cathode current was particularly sensitive to
the polymer grid (3) to anode (1) voltage, V_G, at V_{AC}
between ± 10V, where V_{AC} is the voltage applied between
25   the anode and the cathode (positive voltage corresponds
to the Au electrode negative with respect to the ITO
electrode).

In Fig. 24, the current between anode and cathode
(I_{AC}) is plotted as a function of the voltage between
30   the polymer grid electrode (3) and the anode (1).
Larger negative grid to anode voltages (V_G) suppress
the hole current.

Similar results were obtained with different
series resistance values in the polymer grid circuit.
35   Thus, the three-terminal device can be operated with

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the polymer grid biased at constant voltage or with the polymer grid drawing significant grid current.

This Example demonstrates that the polymer grid triode functioned as a three-terminal device; the anode-cathode current was controlled by the voltage between the anode and the polymer grid electrode. The Example also demonstrates that different blends can be used to fabricate the porous PANI network (PMMA in Example 11 and PES in Example 10).

Example 12:

A polymer grid light-emitting triode in the general configuration of Fig. 1 and the more specific configuration of Fig. 25 was fabricated using the following materials for the indicated layers and constituents:

Substrate (10): Glass

1st electrode (1): ITO

First active electronic material (2): Poly(vinyl carbazole), PVK. The PVK film (1000Å) was cast from cyclopentanone directly onto the ITO electrode.

Polymer grid electrode (3): Polyaniline filled with MEH-PPV (3') (300Å); the filled network was made in a single step using an initial PANI:PMMA blend containing 5% PANI using toluene at the solvent. The filled network was fabricated directly onto the PVK second active electronic material layer (2) using the method described in Example 1.

Third active electronic material (4): MEH-PPV (1400Å) cast onto the filled network, (3) and (3')

2nd electrode (5): Calcium (Ca) metal (1500Å) was deposited onto the third layer by vacuum evaporation.

The device was connected such that forward anode-cathode bias corresponds to the anode (1) positive with respect to the Ca cathode (5). The conducting polyaniline network polymer grid electrode

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(3) was electrically connected to an external battery circuit such that a voltage was applied between the conducting network and the ITO electrode (1).

The anode-cathode current vs voltage (I_{AC} vs V_{AC}) curves are shown for different voltages (V_G) between the anode and the polymer grid electrode in Fig. 26. The data in Fig. 26 demonstrate control of the anode-to-cathode current by the application of a voltage between the polymer grid and the anode. Fig. 26 demonstrates that the structure functions as a three-terminal device.

Fig. 27 shows the light emitted from the polymer grid triode as a function of the anode-to-cathode voltage (V_{AC}) for several different grid-anode bias voltages (V_G). The light emitted was controlled by the grid voltage. This control is shown directly in Fig. 28, where the light emitted at constant V_{AC} (for V_{AC} = 2V, 5V and 6.5V) is plotted as a function of V_G. Fig. 28 demonstrates that the emitted light level can be varied by more than two orders of magnitude by changes in the polymer grid voltage.

When the polymer grid is biased positive with respect to the anode, a potential well for electrons was formed, since the electron energy is minimum when the electrons are near the polymer grid electrode. This potential well served to control the balance between the electron and hole currents and thereby increase the performance of the light-emitting triode.

Similar results were obtained with different series resistance values in the polymer grid circuit (1MΩ or 100KΩ; the resistance from anode to cathode was approximately 100KΩ). Thus, the three-terminal device can be operated with the polymer grid biased at constant voltage or with the polymer grid drawing significant grid current.

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This Example demonstrates the polymer grid light-emitting triode; the intensity (brightness) of the emission is controlled by the voltage applied between the polymer grid and the anode. The Example also shows

5   that the biasing of the polymer grid served to control the balance between the electron and hole currents and thereby increase the performance of the light-emitting triode

Example 13:

10   A polymer grid triode in the general configuration of Fig. 1 and the more specific configuration of Fig. 29 was fabricated using the following materials for the indicated layers and constituents:

Substrate (10): Glass

15   1st electrode (1): ITO

First active electronic material (2) Poly(vinyl carbazole), PVK. The PVK film (1500Å) was cast from cyclopentanone directly onto the ITO electrode.

Polymer grid electrode (3): Polyaniline filled

20   with MEH-PPV (300Å) (3'); the filled network was made in a single step using an initial PANI:PES blend containing 40% PANI. The filled network was fabricated directly onto the PVK first active electronic material layer (2) using the method described in Example 1.

25   Third active electronic material (4): MEH-PPV (1400Å) cast onto the filled network, (3) and (3').

2nd electrode (5): Gold (Au) metal deposited onto the third layer by vacuum evaporation.

The device was connected such that forward

30   anode-cathode bias corresponds to the anode (1) positive with respect to the Au electrode (5). The conducting polyaniline polymer network electrode was electrically connected to an external battery circuit including battery 12 and 1 mohm resistor 14 such that a

35   voltage V_G was applied between the polymer grid 3 and

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the electrode 5 *opposite* to the substrate. The
anode-cathode current vs voltage curves (I_{AC} vs V_{AC}) are
shown for different voltages V_G between the anode and
the polymer grid electrode in Fig. 30.

5   The polymer grid triode studied in this Example
was a single carrier device, since electron injection
from the Au electrode was negligible. The
anode-to-cathode current was particularly sensitive to
the polymer grid (3) to Au (5) voltage.

10   Similar results were obtained with different
series resistance values in the polymer grid circuit
(1MΩ or 100KΩ; the resistance from anode to cathode was
approximately 100KΩ). Thus, the three-terminal device
can be operated with the polymer grid biased at

15   constant voltage or with the polymer grid drawing
significant grid current.

           This Example demonstrates that the polymer grid
triode functioned as a three-terminal device; the
anode-cathode current was controlled by the voltage

20   between the electrode (5) *opposite* to the substrate
(10) and the polymer grid electrode 3.

Example 14:
           A polymer grid triode in the configuration of Fig.
1 was fabricated using the following materials for the

25   indicated layers and constituents:
           Substrate (10): Glass
           1st electrode (1): ITO
           First active electronic material (2) Poly(vinyl
carbazole), PVK. The PVK film (1500 Å) was cast from

30. cyclopentanone directly onto the ITO electrode.
           Polymer grid electrode (3): Polyaniline filled
with 5% PMMA (3'); in this Example, the PMMA was not
removed from the PANI:PMMA blend. The filled network
blend was fabricated directly onto the PVK first active

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electronic material layer (2) using the method described in Example 1.

Third active electronic material (4): MEH-PPV cast onto the filled network, (3) and (3').

2nd electrode (5): Calcium (Ca) metal deposited onto the third layer by vacuum evaporation.

The I_{AC} vs V_{AC} curves were determined and are plotted in Fig. 31 for various voltages applied to the PANI grid electrode. The top curve is at $V_G = -8.5V$, the middle is at $V_G = 0.V$ and the lower curve is at $V_G = 15V$. I_{AC} vs V_{AC} curves are plotted in Fig. 32 for a similar device but with the PMMA removed and replaced by MEH-PPV (in a single step) using toluene as the solvent. Although the I-V characteristics are similar for the two devices, leaving the PMMA in the grid resulted in reduced sensitivity to the grid voltage as evidenced by the fact that the grid voltage for the top curve in Fig. 32 was only -4.8V, the middle was 0V and the lower curve was at 4.4V.

This example demonstrates the importance of removing the host polymer from the PANI:host blend so as to provide better contact of the PANI network to the active electronic material.

Example 15:

A polymer grid light-emitting triode in the configuration of Fig. 1 was fabricated using the following materials for the indicated layers and constituents:

Substrate (10): Glass

1st electrode (1): ITO

First active electronic material (2) Poly(vinyl carbazole), PVK. The PVK film (1000 Å) was cast from cyclopentonone directly onto the ITO electrode.

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Polymer grid electrode (3): Polyaniline (100%).
The 100% PANI layer was cast directly onto the PVK
first active electronic material layer (2).

Third active electronic material (4): MEH-PPV
cast onto the 100% PANI grid, (3).

2nd electrode (5): Calcium (Ca) metal deposited
onto the third layer by vacuum evaporation.

The device was connected such that forward anode-
cathode bias corresponds to the anode (1) positive with
respect to the Ca cathode (5). The conducting
polyaniline network polymer grid electrode (3) was
electrically connected to an external battery circuit
such that a voltage was applied between the conducting
network and the ITO electrode (1).

The device described in this Example was in every
way similar to that described in Example 12 with a
single exception: in this Example 15, the grid
electrode was 100% PANI while in Example 12, the
polymer grid electrode was a PANI network filled with
MEH-PPV.

The I_{AC} vs V_{AC} and light output vs V_{AC}, for various
V_G, are shown in Figs 33 and 34 respectively. Note
that with 100% PANI as the polymer grid electrode, the
I_{AC} vs V_{AC} curves and the light output vs V_{AC} curves are
insensitive to V_G. The data shown in Fig. 33 were
gathered at V_G values of -5V, OV and -5 but all fell on
a single curve. This same effect was observed in the
data plotted in Fig. 34.

This Example demonstrates the importance of the
high surface area, electric field enhancing PANI
network in contact with the active electronic material
(MEH-PPV in this Example).

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Example 16:

A polymer grid triode in the configuration of Fig. 1 was fabricated using the following materials for the indicated layers and constituents:

5
    Substrate (10): Glass

    1st electrode (1): Gold (Au)

    First active electronic material (2):

        Poly(vinyl carbazole), PVK. The PVK

        film ($\approx$1000Å) was cast from meta-cresol

10
        directly onto the Au (on glass) electrode.

    Polymer grid electrode (3): Polyaniline filled will MEH-PPV (3'); the filled network was made in a single step using an initial PANI:PES blend containing 25% PANI. The filled network was fabricated directly

15
onto the PVK first active electronic material layer (2) using a method described in Example 1.

    Third active electronic material (4): MEH-PPV

        cast onto the filled network, (3) and (3').

    2nd electrode (5): Gold (Au) metal deposited

20
        onto the third layer by vacuum evaporation.

Because of the built-in potentials, Au more electronegative than PANI, this configuration is analogous to a pnp-transistor.

The experimental results are summarized in

25
Fig. 35; I_{AC} vs V_{AC} curves are plotted at V_G=0 (zero grid current) top curve and at V_G=0.07V with I_G=0.1 mA bottom curve. The effect of the grid current on I_{AC} is evident at all V_{AC} bias levels.

Note that the grid to anode resistance was

30
approximately 700 ohms, while the anode to cathode resistance under forward bias (V_{AC}=8 V) was approximately 30,000 ohms. Thus, the PVK layer dominated the anode to cathode current (I_{AC}).

The data summarized in Fig. 35 indicate that

35
current in the external circuit can be switched by the device; application of 0.1 mA grid current (I_G)

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results in an increase in I_{AC} by significantly more than
0.1 mA; the change in I_{AC} is 0.17 mA at V=8 V, nearly a
factor of two greater than the input grid current.
Because the current was limited by the high series
5   resistance of the PVK layer, the data indicated that
higher current would be switched by using a conjugated
polymer layer (such as P3OT or PPV) as the first
electronically active material (2).

          Using this polymer grid triode in an external
10   circuit with a series resistor (R_s) in the anode circuit
resulted in voltage gain. For example, with R_s=10,000
ohms, the change in the voltage across R_s was 1.7 volts.
Since the applied V_G was 0.07 V, the voltage gain was
≈25.

15   This Example demonstrates that polymer grid
triodes operate as three terminal devices, analogous to
pnp transistors. The Example demonstrates both current
gain and voltage gain from polymer grid triode devices.

Example 17:
20   An Al/MEH-PPV/PANI-CSA/MEH-PPV/Ca polymer grid
triode was fabricated. The Al anode (1) was first
vacuum deposited onto a glass substrate (10). The
first MEH-PPV layer (2) was then spin-cast from
solution in xylene. To make the polymer grid (3), the
25   PANI-CSA blends were spin-cast directly onto the first
MEH-PPV layer. To fabricate the filled network grid
electrode 3', MEH-PPV was spin-cast at 1000 rpm from
solution in xylene directly onto the thin film of the
PANI:PES blend. Since xylene is an excellent solvent
30   for PES, the PES in the PANI:PES blend was etched out
by the xylene and subsequently carried away by the
excess MEH-PPV solution during the spin-casting
process. Hence, in a single step, MEH-PPV replaced PES
to fill (or partially fill) the voids in the porous
35   structure within the PANI:PES network. The MEH-PPV

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layer extended beyond the filled network to form the
third active electronic material, layer (4) in Fig. 1.

The polymer grid triode device was completed by
vacuum deposition of the thin metallic cathode film 5
5   by vapor deposition. The polymer grid triode thus had
continuous semiconducting polymer between anode and
cathode with the PANI-CSA grid network in a thin layer
within the polymer semiconductor.

The I_{AC} vs V_{AC} characteristics of an Al/MEH-
10   PPV/PANI-CSA/MEH-PPV/Ca polymer grid TFT are shown in
Fig. 36 for eight grid voltages, V_G, applied between
the PANI-CSA network grid and the Al cathode and
ranging from 30V to -50V. In this case, the PANI-CSA
grid was fabricated from a 3% PANI-CSA:PES blend, so
15   the network is relatively dilute. For $V_G = 0$, the I_{AC}
vs V_{AC} curve is like that of a diode; current flows
when the Al cathode is biased negative with respect to
the Ca anode. The Al/MEH-PPV/Ca configuration is a
single carrier (electron-only) device; electrons are
20   injected at the Al electrode and withdrawn at the Ca
electrode. As the PANI grid was made more and more
negative with respect to the Al and Ca electrodes (V_G
negative), the electron current is suppressed. For
example, with $V_G = -9.7$ V, $I_{AC} = 0$ until the magnitude
25   of V_{AC} exceeds 10V. More generally, we found that with
$V_G = -V_0$, $I_{AC} = 0$ until the magnitude of V_{AC} exceeds
(approximately) V_0.

When $V_G > 0$, however, the injected electrons are
withdrawn at the positively biased PANI-CSA grid. In
30   addition, under such forward bias conditions for the
PANI-CSA/MEH-PPV/Ca diode, holes are injected at the
PANI-CSA/MEH-PPV interface. In fact, as would be
expected for V_G positive (i.e. PANI-CSA positive with
respect to Ca), the PANI-CSA/MEH-PPV/Ca diode emits
35   light. This emission has been characterized in detail
in a series of separate experiments using ITO/MEH-

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PPV/PANI-CSA/MEH-PPV/Ca polymer grid triodes (the
transparent ITO facilitates the detection of the
emitted light.)

5
Qualitatively, the I_{AC} vs V_{AC} characteristics shown
in Fig. 36 are consistent with the electronic structure
diagrams of Fig. 2. For $V_G < 0$, electrons which are
injected at the Ca cathode pass through the PANI-CSA
grid and are collected at the Ca electrode as long as
$|V_{AC}| > |V_G|$. Thus, the PANI-CSA network is

10
sufficiently dilute to allow electron current to flow
and to function as a control grid.

Independent measurements of the I vs V curves for
the A1/MEH-PPV/PANI-CSA half of the device and for the
PANI-CSA/MEH-PPV/Ca half of the device show that both

15
exhibit the expected diode behavior. The data are
shown in Fig. 37. Although the rectification ratios
are moderate (<100), both the A1/MEH-PPV/PANI-CSA half
and the PANI-CSA/MEH-PPV/Ca half yield diode-like I-V
curves. (Top curve and bottom curve in Fig 37,

20
respectively.)

The electronic structure diagrams of Fig. 2 imply
that I_{AC} will begin to flow when the PANI-CSA/MEH-PPV/Ca
is in the flat band condition. Fig. 38 shows that for
successively higher values of $|V_G|$, the steep onset of

25
I_{AC} (which defines the flat band condition) moves to
proportionally to higher values of $|V_{AC}|$. Again, the
results are as expected from the electronic structure
diagrams sketched in Fig. 2.

Fig. 39 shows the current gain, $G = \Delta I_{AC} / \Delta I_G$, of

30
an A1/MEH-PPF/PANI/MEH-PPV/Ca device, where ΔI_G is the
change in grid current and ΔI_{AC} is the corresponding
change in current in the anode-to-cathode circuit. The
polymer grid triode used to obtain the data shown in
Fig. 39 contained a PANI-CSA network grid fabricated

35
from a blend with initial PANI-CSA concentration of 3%.
The test circuit used to make those measurements is

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shown in Fig 40 an external AC signal (Vs = 5v peak-to-peak) was applied in the grid circuit with the grid biased at V_G = -7.5 V(DC) and V_{AC} = -12 V; the test circuit is shown in the inset. As a result, AC current flowed into the grid circuit (and was directly measured by an ammeter connected to the grid), thereby modulating the grid voltage. The resulting change in I_{AC} determined the gain.

As shown in Fig. 39, at low frequencies G ≈ 4.5, consistent with estimates based on the change in the dc characteristics at different V_G. Upon increasing the modulation frequency, f, the gain is observed to fall to one-half the low frequency value at f ≈ 400 Hz (ω ≈ 2.4×10^3 rad/s), indicating a response time τ ≈ 4×10^{-4} s.

The high frequency response shown in Fig. 39 is limited by the RC time constant of the device. The input resistance to the PANI-CSA grid is determined by the resistance of the PANI-CSA network; $-R_s = \rho_s L/Ld$, where ρ_s is the resistivity of the network, and L and d are, respectively, the length (lateral dimension) and thickness of the device. The capacitance is determined by the thin film ("capacitator") geometry, $C = \varepsilon_s$ is the dielectric constant of the semiconductor. Thus

$$\tau_{RC} = RC = \rho_s \varepsilon_s (L/d)^2.$$

The measured values of R_s and C are consistent with the high frequency cut-off shown in Fig. 39. Since the dimensions of the devices fabricated in this initial study were of order 0.5 cm, reduction of the device dimensions would increase the RC-limited frequency response; for example, by decreasing the lateral dimensions to 10 μm, $1/\tau_{RC}$ >>10^8 Hz.

The theoretical limit for the high frequency cutoff can be simply estimated from the mobility of the semiconducting polymer. To obtain significant gain, carriers must move through the grid in a time comparable with the period of the ac signal. The

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carrier velocity is given by $2\mu V_G/d$, where μ is the mobility and d is the thickness of the device (e.g. 2000Å). Thus, the intrinsic response time, τ_i, (i.e. that limited by the mobility of the semiconducting

5   polymer) is given by

$$\tau_i, \approx d_2/\mu V.$$

Assuming $\mu \approx 10^{-4}$ cm^2/V-s for the disordered polymer film cast from solution and taking $V_G = 5$ V, we estimate $\tau \approx 10^{-6}$ s. This short response time is a direct result

10   of the thin film architecture of the polymer grid triode. The implied high frequency response is quite remarkable for a transistor-like device made with such a low mobility material.

         Higher gain can be achieved by improving the

15   rectification ratios of the back-to-back diodes, by making the overall structure (and the component layers) thinner, and by optimizing the concentration of PANI-CSA in the network for optimum transmission of carriers through the network grid and for optimum input

20   resistance to the grid.

         This example demonstrates that polymer grid triodes can be fabricated by processing the component materials from solution. The polymer network grid can be used to control the current flow from anode-to-

25   cathode, thereby creating a new class of transistor-like devices which exhibit current gain (and voltage gain).

Claims:

1.   A polymer grid comprising a body of electrically conducting organic polymer, said body having an open and porous network morphology and defining an expanded surface area void-defining porous network and active electronic material located within at least a portion of the void spaces defined by the porous network.

2.   The polymer grid of claim 1 wherein the active electronic material is a semiconductor.

3.   The polymer grid of claim 1 wherein the active electronic material is inorganic.

4.   The polymer grid of claim 1 wherein the active electronic material is organic.

5.   The polymer grid of claim 4 wherein the active electronic material comprises nonconjugated organic polymer.

6.   The polymer grid of claim 5 wherein the active electronic material comprises conjugated organic polymer.

7.   The polymer grid electrode of claim 5 wherein the active electronic material is a low molecular weight semiconducting oligomeric material selected from the group consisting of oligomers of thiophene, pyrrole, phenylene, phenylene vinylene and derivative thereof.

8.   The polymer grid of claim 1 wherein the body is a thin film.

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9.   The polymer grid of claim 8 wherein the thin
film is less than 200 nanometers thick.

10.   A polymer grid electrode comprising a body of
electrically conducting organic polymer electrically

5   joined to an electrical connector, said body having an
open and porous network morphology and defining an
expanded surface area void-defining porous network.

11.   The polymer grid electrode of claim 10
additionally comprising a active electronic material

10   selected from organic and inorganic semiconductors
located within at least a portion of the void spaces
defined by the porous network.

12.   A polymer grid triode comprising a first
electrode and a second electrode spaced apart from one

15   another with a polymer grid comprising a body of
electrically conducting organic polymer said body
having an open and porous network morphology and
defining an expanded surface area void-defining porous
network interposed between the first electrode and the

20   second electrode.

13.   The polymer grid of claim 1, electrode of
claim 10 or triode of claim 12 wherein the conducting
organic polymer comprises conducting polypyrolle or
polyaniline.

25   14.   The polymer grid of claim 1, electrode of
claim 10 or triode of claim 12 wherein the conducting
organic polymer comprises polyaniline in the
conducting, protonated emeraldine salt form.

15.   The polymer grid of claim 1, electrode of
30   claim 10 or triode of claim 12 wherein the expanded

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surface area is a surface area greater than 10 cm^2/gram and the void space is at least 1% by volume.

16.   The polymer grid triode of claim 12 wherein the body is a thin film having a thickness such that the total distance between the first electrode and the second electrode is less than a micron.

17.   The polymer grid triode of claim 12 additionally comprising active electronic material between at least one of the first and second electrodes and the polymer grid.

18.   The polymer grid triode of claim 12 additionally comprising active electronic material selected from organic and inorganic semiconductors located within at least a portion of the void spaces defined by the porous network.

19.   The polymer grid triode of claim 18 additionally comprising active electronic material between at least one of the first and second electrodes and the polymer grid.

20.   The polymer grid triode of claim 19 wherein the active electronic material between the electrodes comprises semiconducting polyaniline, polyaniline in the conducting protonated emeraldine salt form, semiconducting polypyrrole, or polypyrrole in the oxidized conducting form.

21.   The polymer grid triode of claim 19 wherein at least one of the active materials comprises a conjugated semiconducting organic polymer or a nonconjugated semiconducting organic polymer.

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22. The polymer grid triode of claim 21 wherein the conjugated polymer is selected from the group consisting of poly(paraphenylene vinylene); a soluble derivative of poly(paraphenylene vinylene); poly(thiophene); a soluble derivative of poly(thiophene) and a low molecular weight semiconducting oligomer of thiophene, pyrrole, phenylene, or phenylene vinylene.

23. The polymer grid triode of claim 19 herein active electronic material is present between the first electrode and the polymer grid.

24. The polymer grid triode of claim 23 wherein the active electronic material comprises a semiconducting polymer.

25. The polymer grid triode of claim 23 wherein the active electronic material comprises a semiconducting hole transport material.

26. The polymer grid triode of claim 23 wherein the active electronic material comprises PVK.

27. The polymer grid triode of claim 19 wherein the active electronic material is present between the second electrode and the polymer grid.

28. The polymer grid triode of claim 27 wherein the active electronic material within the voids and the active electronic material between the electrodes are the same.

29. The polymer grid triode of claim 27 wherein the active electronic material within the voids and the

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active electronic material between the electrodes are
different.

30. The polymer grid triode of claim 27 wherein
the active electronic material between the electrodes
comprises a semiconducting electron transport material.

31. The polymer grid triode of claim 27 wherein
the active electronic material between the electrodes
is part of a bilayer, which bilayer comprises a layer
of active electronic material and a second polymer grid
comprising a second body of electrically conducting
organic polymer, said second body having an open and
porous network morphology and defining an expanded
surface area void-defining porous network and active
electronic material located within at least a portion
of the void spaces defined by the porous network the
active electronic material in the voids of the second
body being different from the active electronic
material between the electrodes.

32. The polymer grid triode of claim 31 wherein
the active electronic material within the voids of the
second body comprises a semiconducting material.

33. The polymer grid triode of claim 12
additionally comprising a substrate selected from a
free standing polymer film, either rigid or flexible,
an inorganic material, an inorganic glass, amorphous
silicon, an inorganic single crystal, single crystal
silicon, single crystal quartz, single crystal
sapphire, and a metal.

34. The polymer grid triode of claim 12, 18 or 19
additionally comprising an electrical connector joined
to said body.

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35. The polymer grid triode of claim 31 additionally comprising an electrical connector joined to one of said first and said second bodies.

36. The polymer grid triode of claim 31 in polymer grid tetrode form additionally comprising electrical connectors joined to said first and second bodies.

37. The polymer grid triode of claim 17, 19 or 23 wherein the active electronic material between the electrodes is a conductor.

38. The polymer grid triode of claim 17, 19 or 23 wherein the active electronic material between the electrodes is a semiconductor.

39. The polymer grid triode of claim 17, 19 or 23 wherein the active electronic material between the electrodes is an inorganic material.

40. The polymer grid triode of claim 17, 19 or 23 wherein the active electronic material between the electrodes is an organic material.

41. The polymer grid triode of claim 40 wherein the active electronic material between the electrodes comprises polyaniline.

42. The polymer grid triode of claim 40 wherein the active electronic material between the electrodes comprises polyaniline in the conductive emeraldine salt form.

43. A polymer grid triode with an electronegative metal as the anode and the cathode and with a polymer

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grid comprising polyaniline in its conducting form and
with semiconducting materials between the anode and the
polymeric grid, between the cathode and the polymeric
grid and within the voids of the polymeric grid, said

5   polymeric grid triode having built-in potentials
analogous to a pnp transistor.

44.   A polymer grid triode with a stable
electropositive metal as the anode and the cathode and
with a polymer grid comprising polyaniline in its

10   conducting form and with semiconducting materials
between the anode and the polymeric grid, between the
cathode and the polymeric grid and within the voids of
the polymeric grid, said polymeric grid triode having
built-in potentials analogous to an npn transistor.

15   45.   A light-emitting polymer grid triode
comprising a first electrode and a second electrode
spaced apart from one another with a polymer grid
comprising a body of electrically conducting organic
polymer said body having an open and porous network

20   morphology and defining an expanded surface area void-
defining porous network interposed between the first
and second electrodes and active luminescent
semiconducting electronic material also interposed
between the first and second electrodes which serves to

25   transport electronic charge carriers between the first
and second electrodes, the carriers being affected by
the polymer grid, such that on applying a turn-on
voltage between the first and second electrodes, charge
carriers are injected and light is emitted.

30   46. The light-emitting polymer grid triode of
claim 45 wherein active electronic material is located
within at least a portion of the void spaces defined by
the porous network.

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47. The light-emitting polymer grid triode of claim 46 wherein the active electronic material located within at least a portion of the void spaces defined by the porous network is the same as the active

5   luminescent semiconducting electronic material.

48. The light-emitting polymer grid triode of claim 46 wherein the active electronic material located within at least a portion of the void spaces defined by the porous network is different than the active

10   luminescent semiconducting electronic material.

49.   The light-emitting polymer grid triode of claim 46 additionally comprising an electrical connector joined to said body and electrically connecting the polymer grid to an external circuit such

15   that a voltage can be applied to the polymer grid electrode and current can be drawn in the grid circuit, either positive or negative, between the polymer grid electrode and one of the other two electrodes so as to function as a three-terminal light emitting triode.

20   50.   The light-emitting polymer grid triode of claim 46 with the turn-on voltage in the forward direction being below 10V.

51.   The light-emitting polymer grid triode of claim 46 wherein the luminescent semiconducting

25   electronic material comprises a low molecular weight semiconducting and/or photoluminescent organic material such as but not limited to the following:
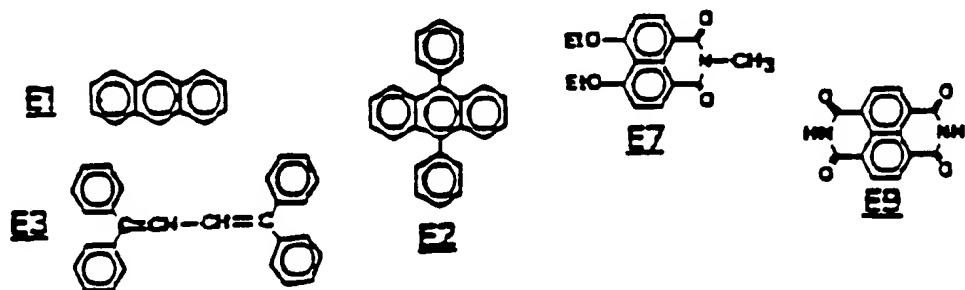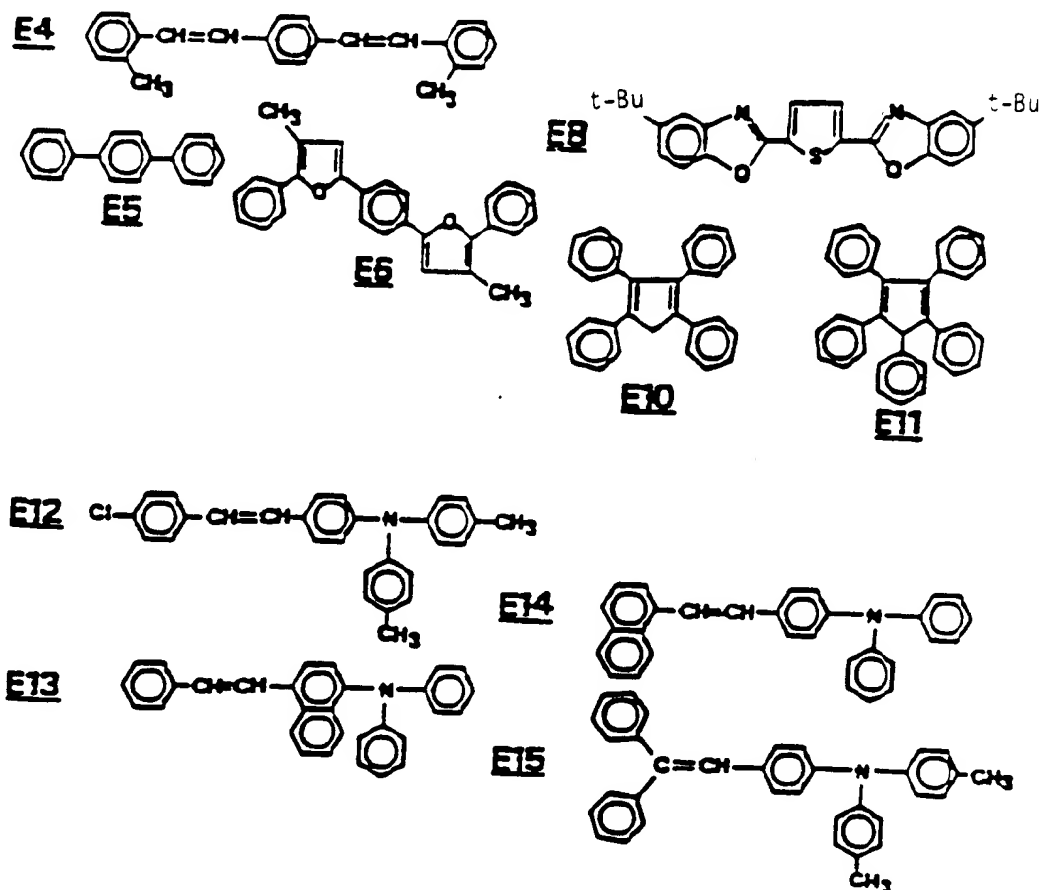
52. The light-emitting polymer grid triode of claim 46 wherein the luminescent semiconducting electronic material comprises a low molecular weight semiconducting oligomer of thiophene, pyrrole, phenylene, and phenylene vinylene.

53. In a circuit in which an electrical current passes between a first electrode and a second electrode separated from one another by an active electronic material capable of transporting electronic charge carriers the improvement comprising an organic polymer grid of claim 1 interposed between said first electrode and said second electrode to affect the active

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electronic material's transporting of electronic charge carriers.

54. The circuit of claim 53 wherein the current results from single carrier injection.

55. The circuit of claim 53 wherein the current results from two carrier injection; electron injection at the first electrode which serves as a cathode and hole injection at the second electrode which serves as an anode.

56. The circuit of claim 53 wherein the network comprising the polymer grid enhances the local electric field upon the application of a voltage between the first electrode and the second electrode, resulting in enhanced charge carrier injection.

57. The circuit of claim 53 wherein the charge carrier injection is enhanced over that without the polymer grid by at least a factor of 5.

58. The circuit of claim 53 wherein the first active electronic material located within the void spaces is the same as the active electronic material separating the first electrode and the second electrode.

59. The circuit of claim 53 wherein the first active electronic material located within the void spaces differs from the active electronic material separating the first electrode and the second electrode.

60. In a circuit in which an electrical current passes between a first electrode and a second electrode

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separated from one another by active electronic
material capable of transporting electronic charge
carriers the improvement comprising a polymer grid
electrode of claim 10 interposed between said first

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electrode and said second electrode, said polymer grid
electrode electrically connected to an external grid
circuit such that a voltage can be applied to the
polymer grid electrode and current can be drawn in the
grid circuit, either positive or negative, between the

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polymer grid electrode and one or both of the first and
second electrodes so as to function as a three-terminal
polymer grid triode and affect the active electronic
material's transporting of electronic charge carriers.

61.   The circuit of claim 60 wherein the first and

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second electrodes are selected to provide rectification
with a rectification ratio greater than 10.

62.   The circuit of claim 60 wherein gain is
achieved.

63.   In a circuit in which an electron current

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passes between an anode and a cathode separated from
one another by an active electronic material capable of
transporting electronic charge carriers the improvement
comprising employing said anode and cathode as elements
of the tetrode of claim 36 with the polymer grid

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electrode electrically connected to an external grid
circuit such that a voltage can be applied to the
polymer grid electrode and grid current can be drawn in
the grid circuit, between the polymer grid electrode
and one or both of the anode and cathode so as to

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affect the active electronic material's transporting of
electronic charge carriers and the second body
electrically connected to a second external circuit
such that a voltage can be applied to the second body

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such that the two external circuits provide independent
control over the electron current and the grid current.

64.   A method for producing a polymer grid of
claim 1 comprising
a. forming a blend comprising bicontinuous
interpenetrating networks of an electrically conducting
polymer and a host polymer, said host polymer being
selectively removable,
b. treating the blend under host polymer-removing
conditions thereby selectively removing the host
polymer leaving a body of electrically conducting
organic polymer, said body having an open and porous
network morphology and defining an expanded surface
area void-defining porous network and
c. placing first active electronic material within at
least a portion of the void spaces defined by the
porous network.

65.   The method of claim 64 comprising:
a. forming a blend comprising bicontinuous
interpenetrating networks of an electrically conducting
polymer and a host polymer, said host polymer being
selectively soluble in a solvent,
b. contacting the blend with the solvent thereby
selectively dissolving the host polymer leaving a body
of electrically conducting organic polymer, said body
having an open and porous network morphology and
defining an expanded surface area void-defining porous
network and
c. placing first active electronic material within at
least a portion of the void spaces defined by the
porous network.

66.   The method of claim 64 wherein steps b. and
c. are separate and serial.

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67.   The method of claim 64 wherein steps b. and
c. are simultaneous.

68.   The method of claim 65 wherein the blend
comprises polyaniline as the conducting polymer.

5   69.   The method of claim 68 wherein the blend
comprises low molecular weight polyester resin or
polymethylmethacrylate (PMMA) as host polymer.
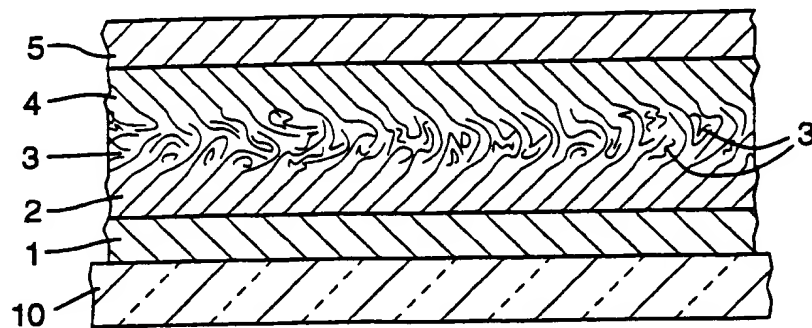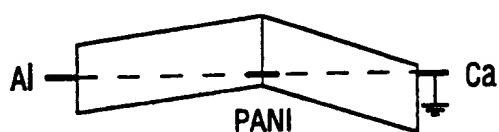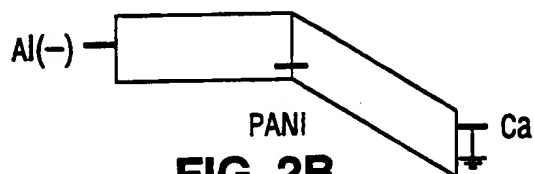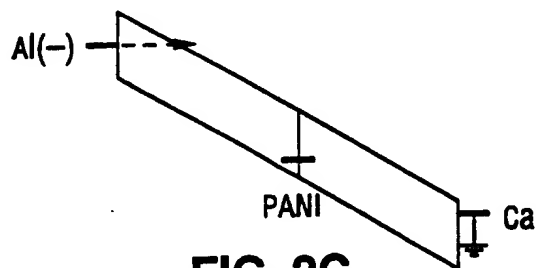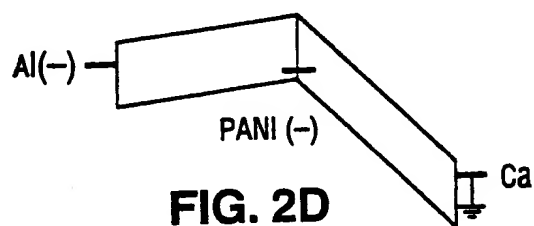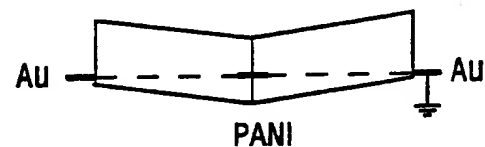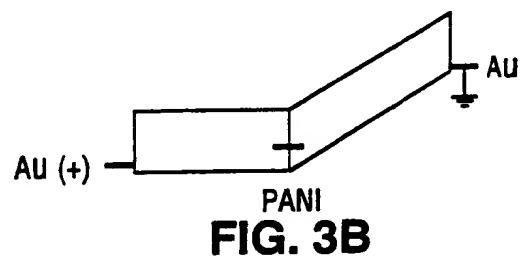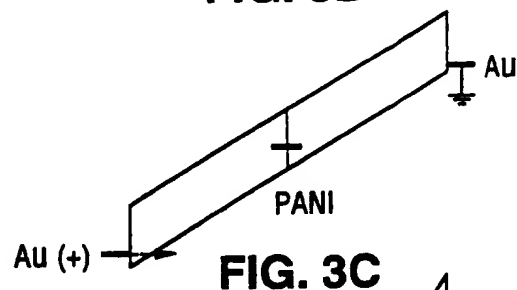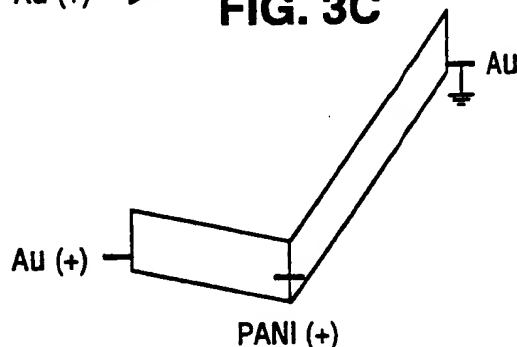
66

FIG. 1

FIG. 2A

FIG. 3A

FIG. 2B

FIG. 3B

FIG. 2C

FIG. 3C

FIG. 2D

FIG. 3D

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FIG. 4

FIG. 5

FIG. 6

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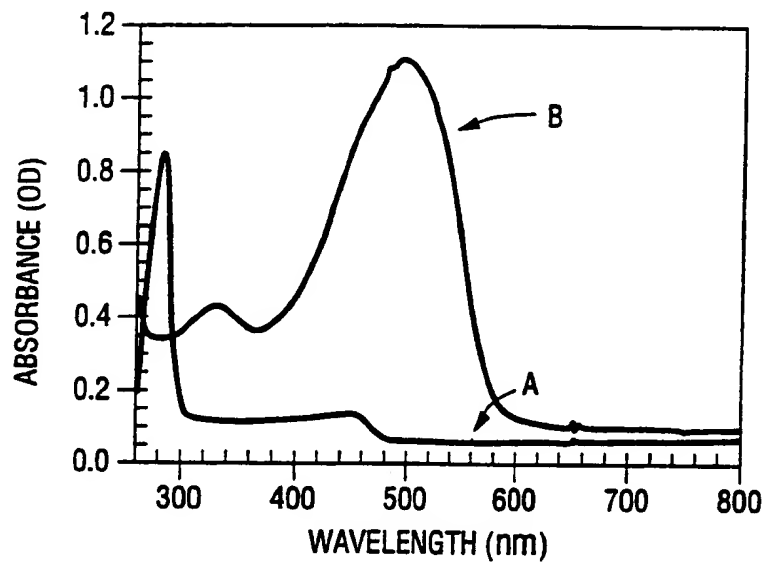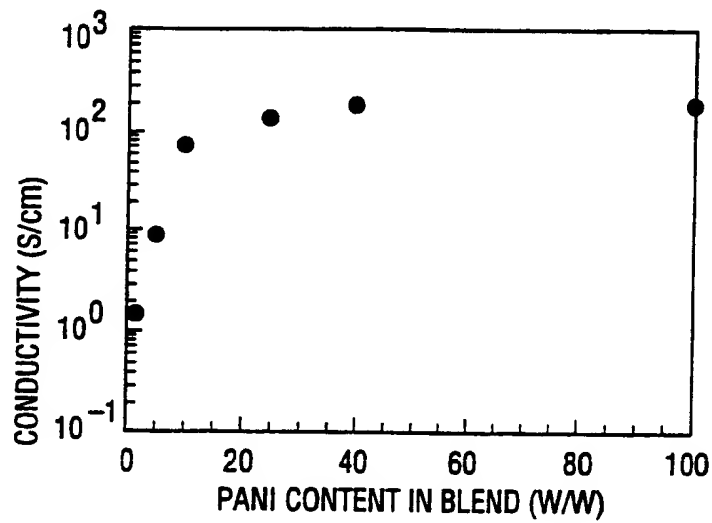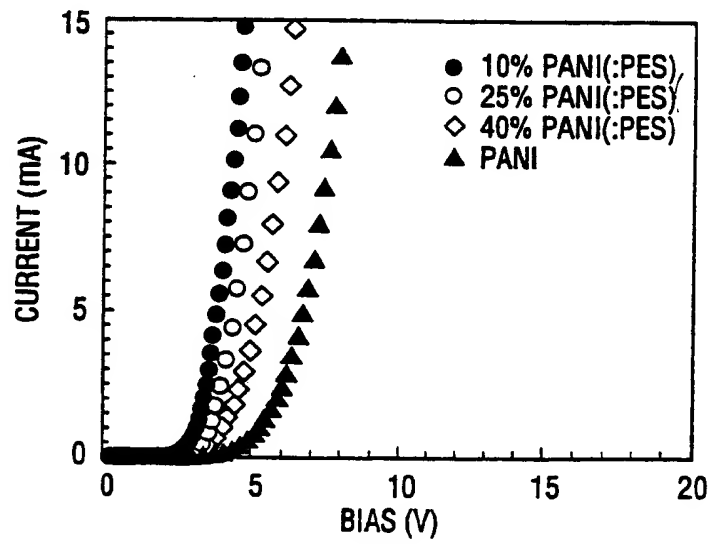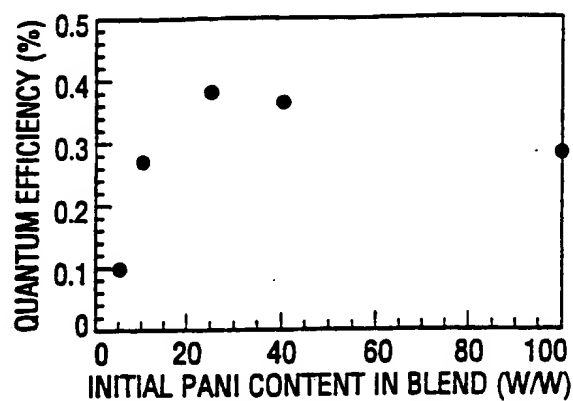
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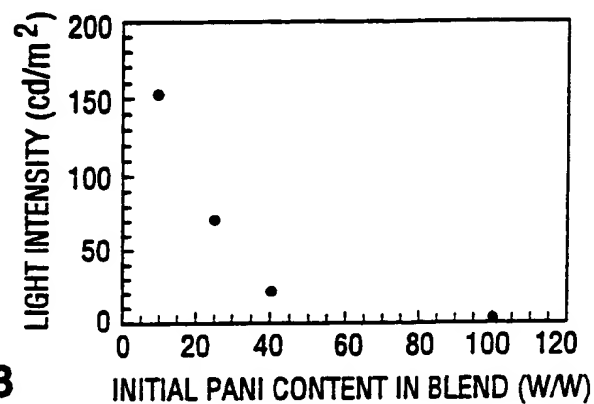
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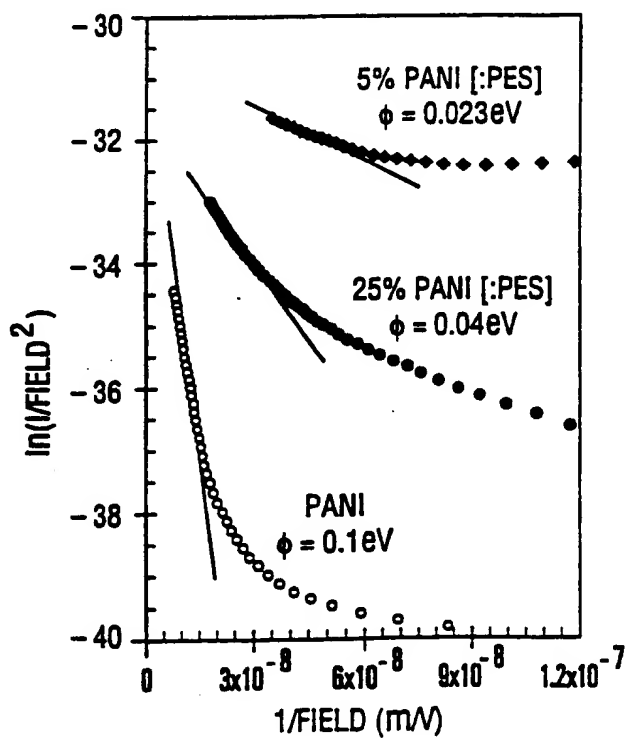
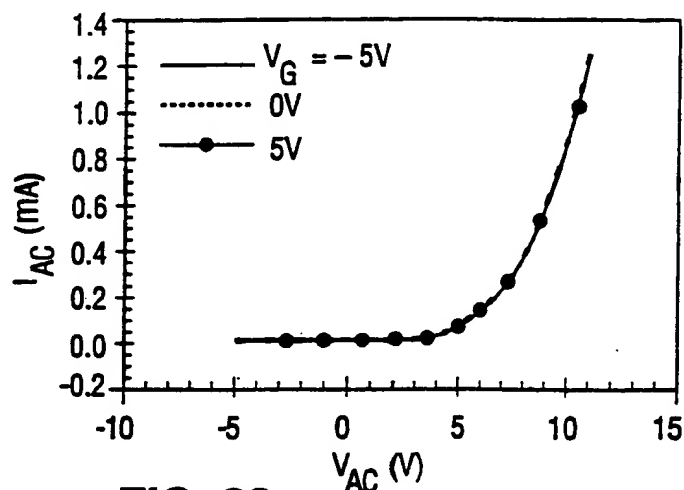FIG. 9

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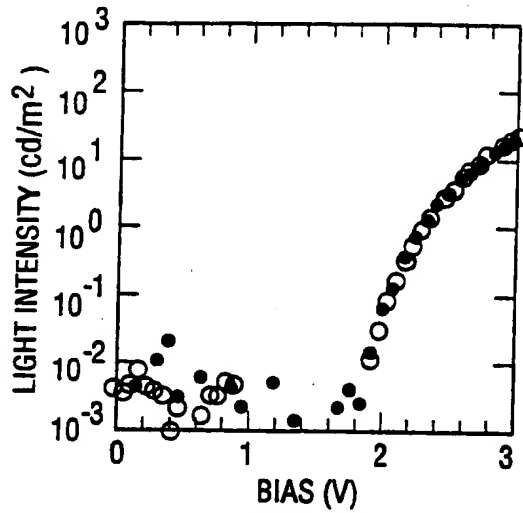
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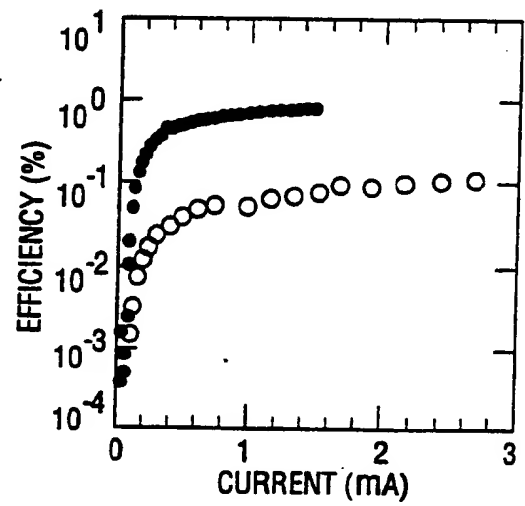
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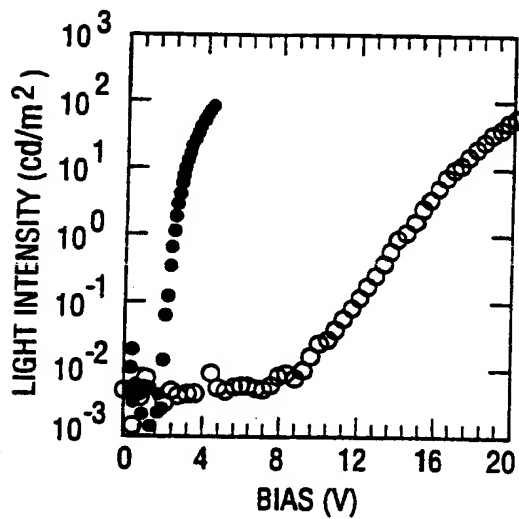
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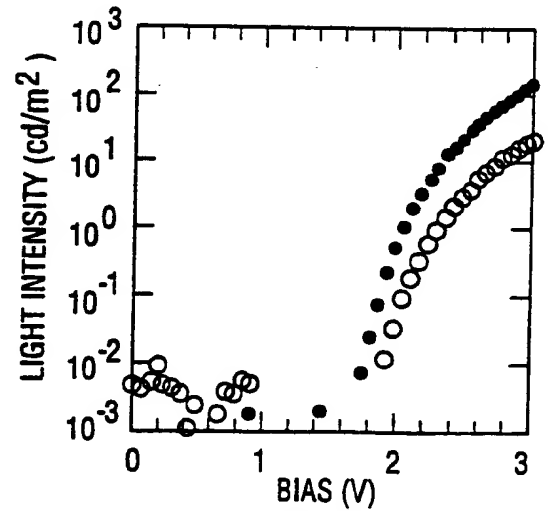
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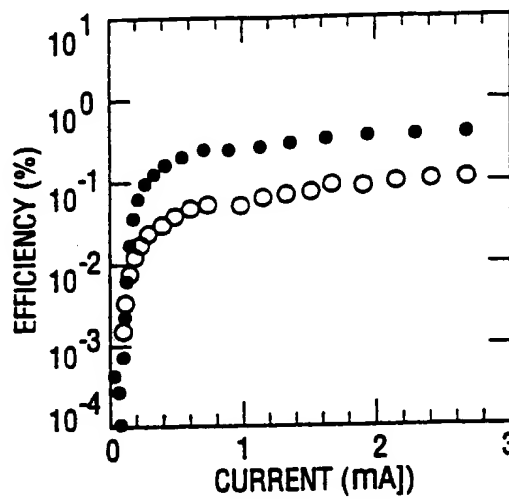
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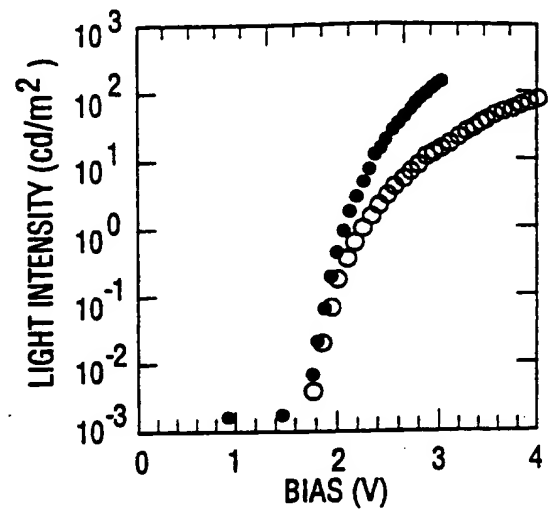
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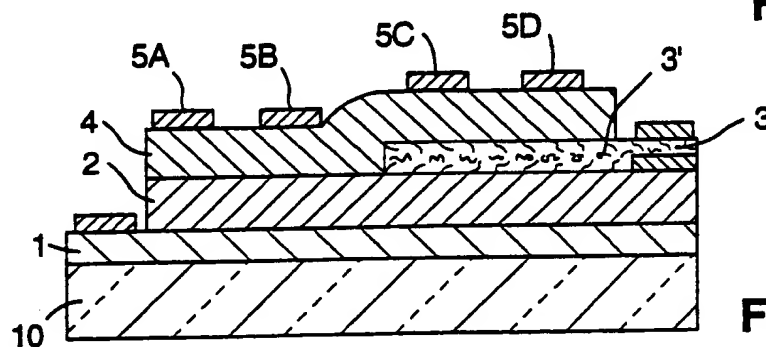
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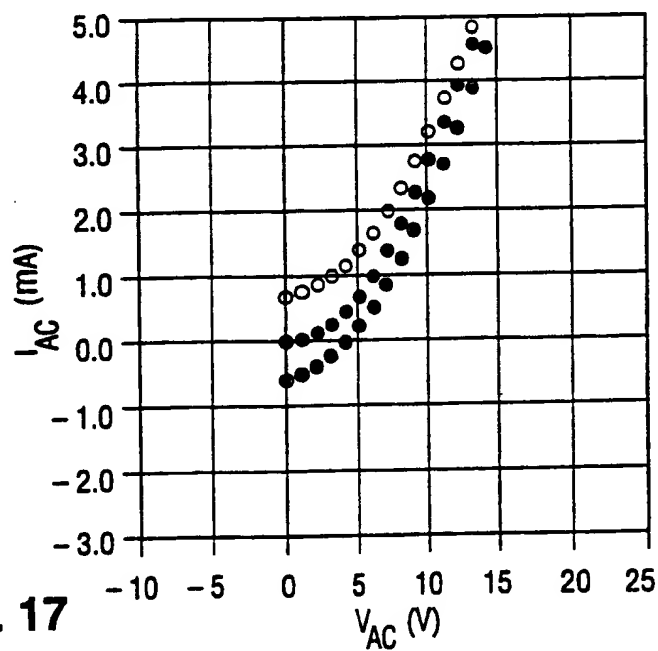
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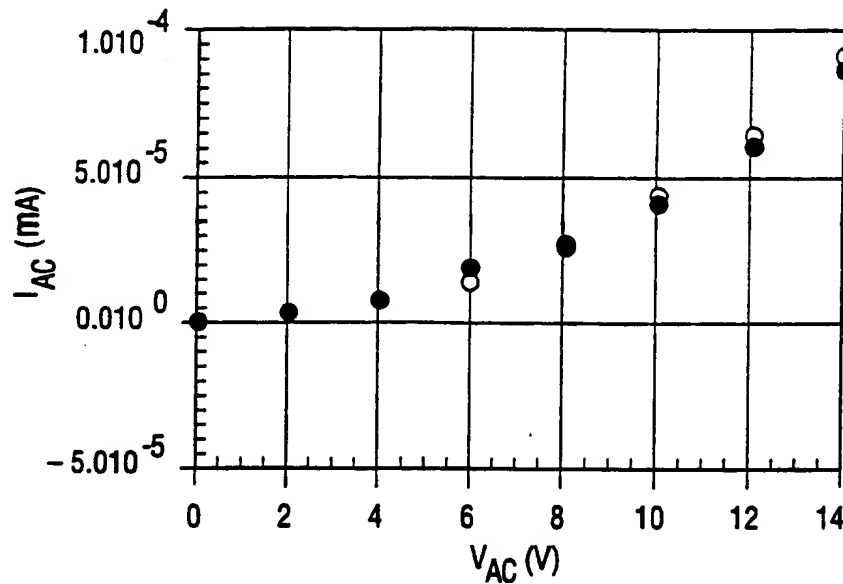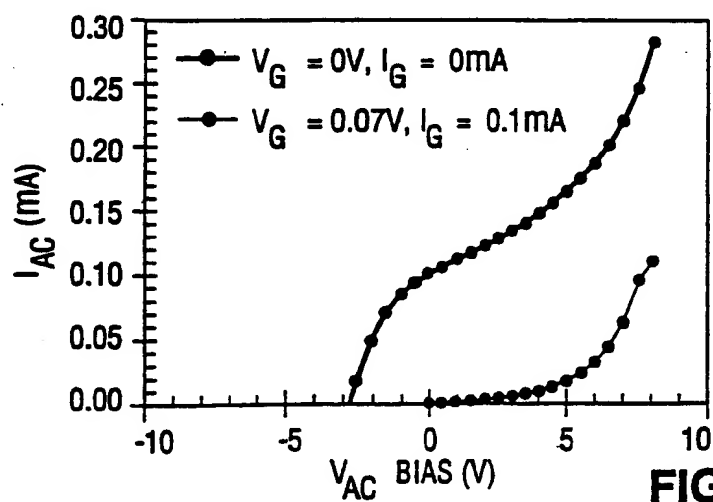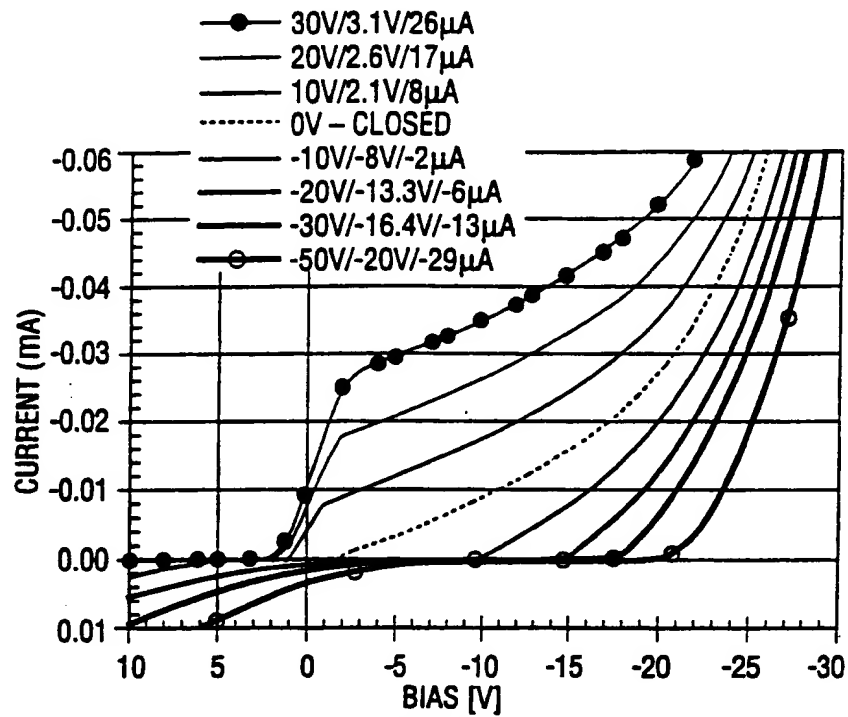
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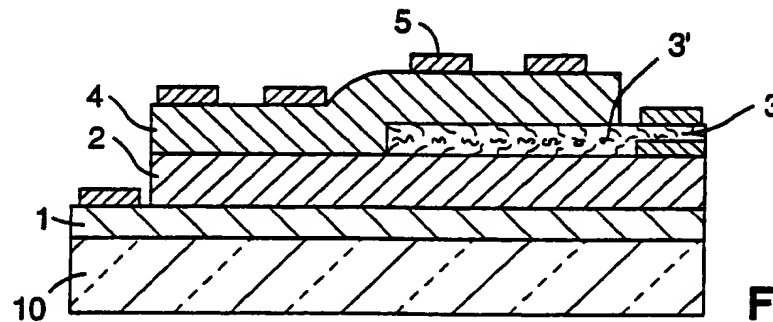
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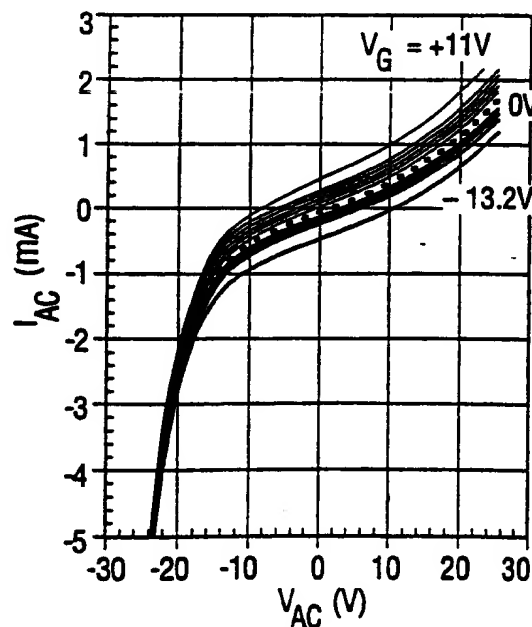
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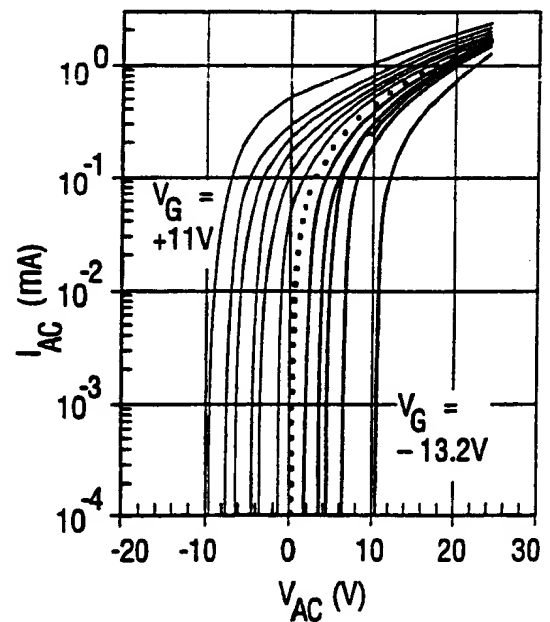
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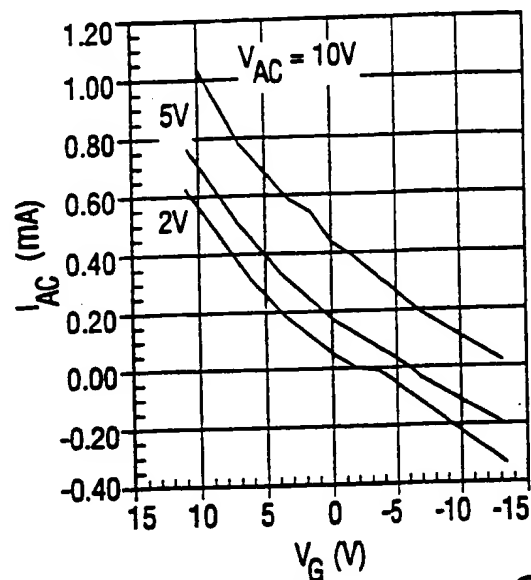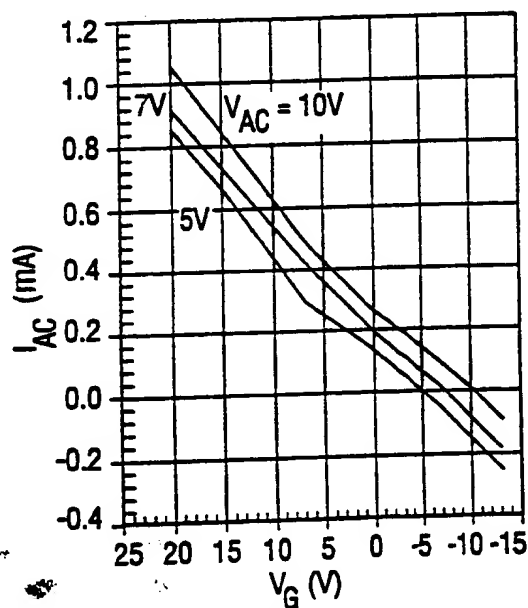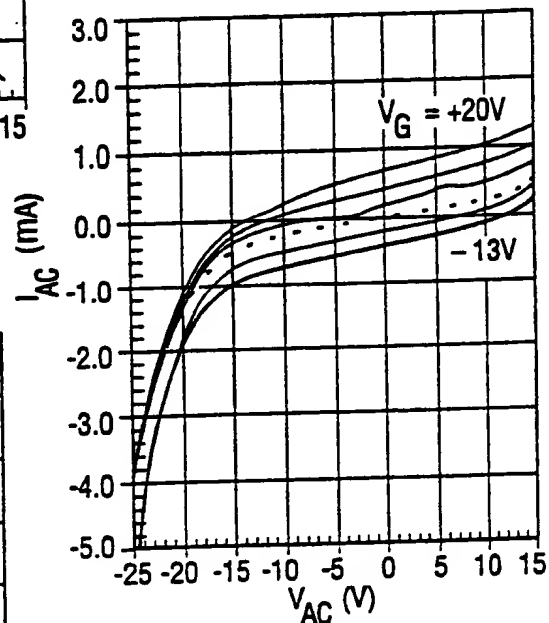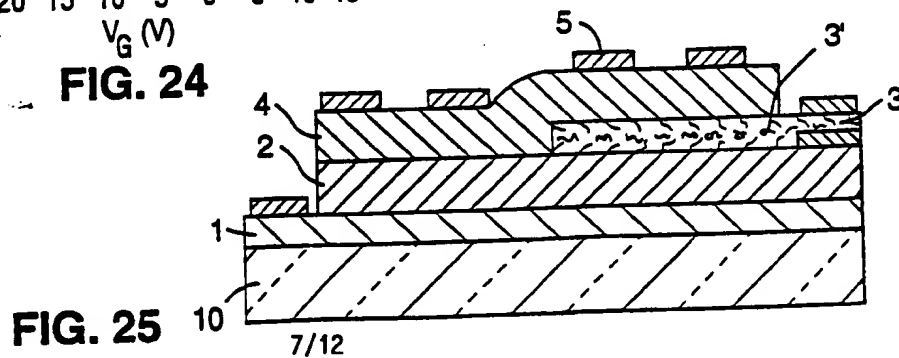
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FIG. 22

FIG. 23

FIG. 24

FIG. 25

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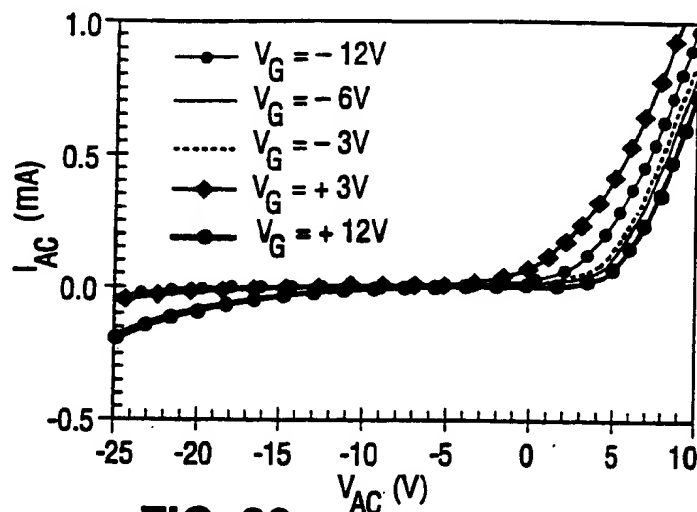
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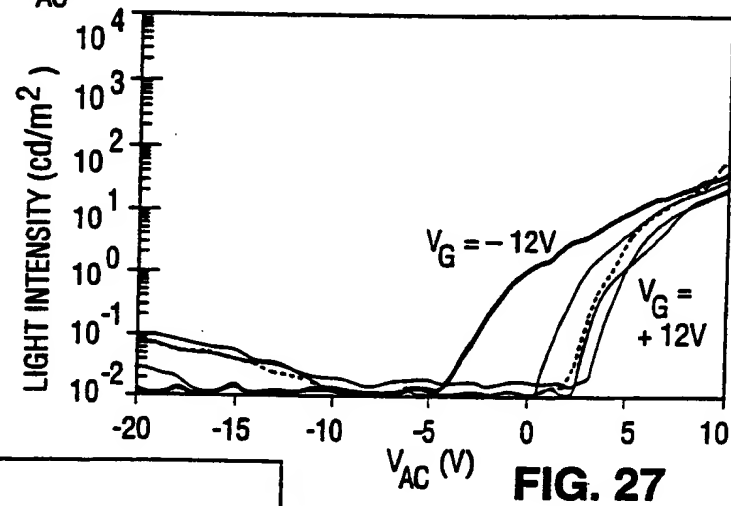
FIG. 27

FIG. 28

FIG. 29

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FIG. 30

FIG. 31

FIG. 32

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FIG. 33

FIG. 34

FIG. 35

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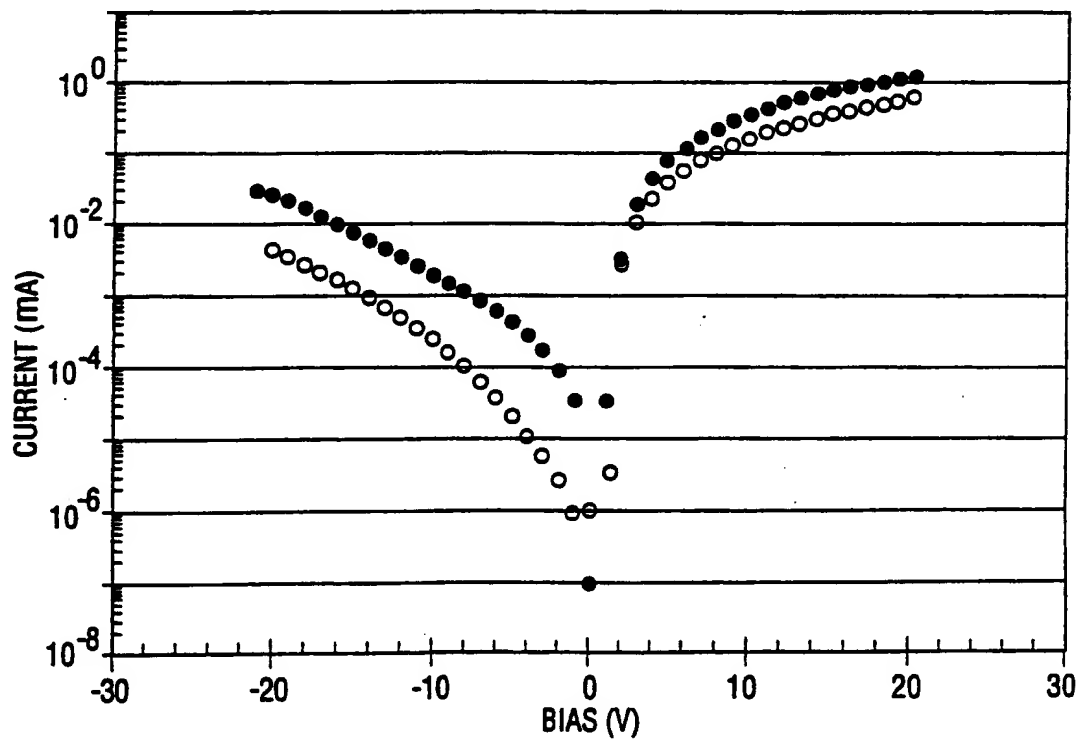RECTIFIED SHEET (RULE 91)
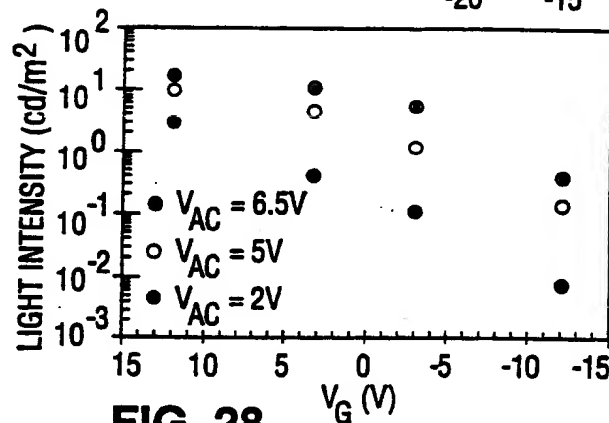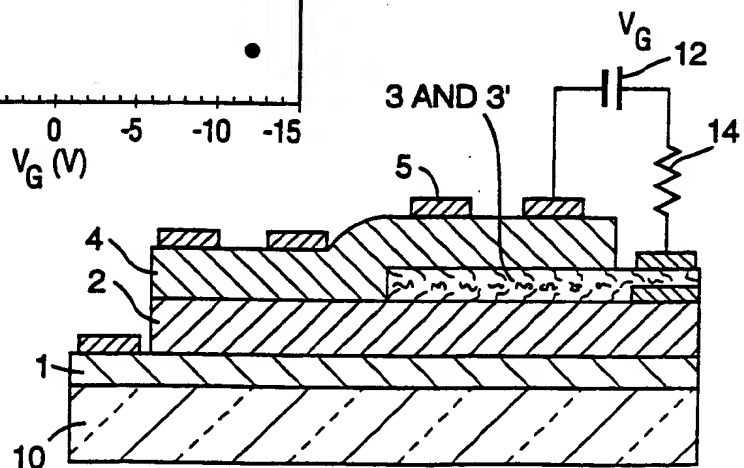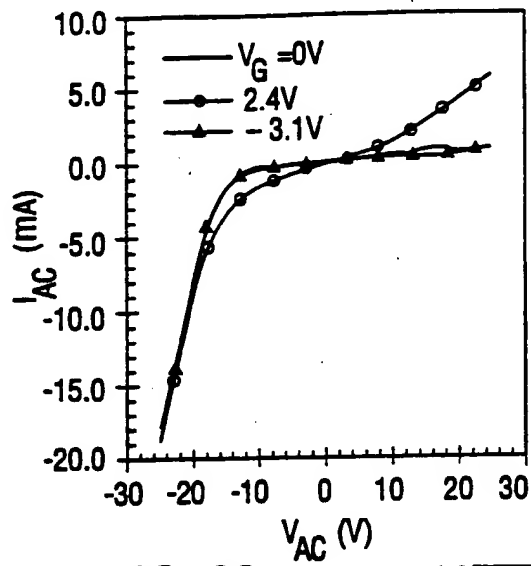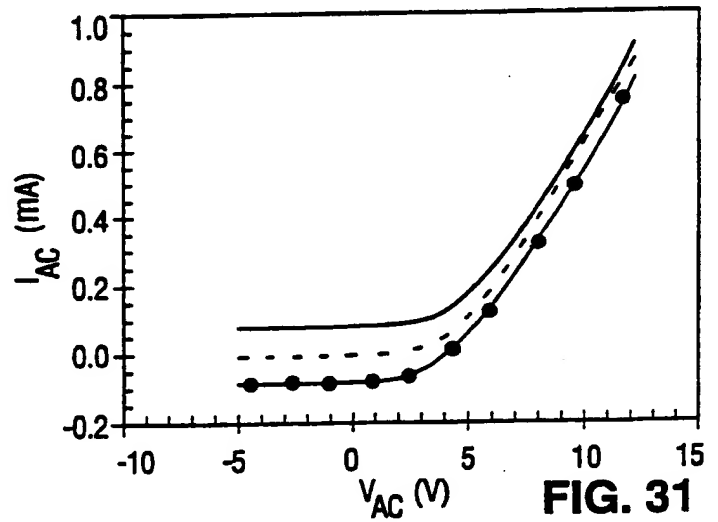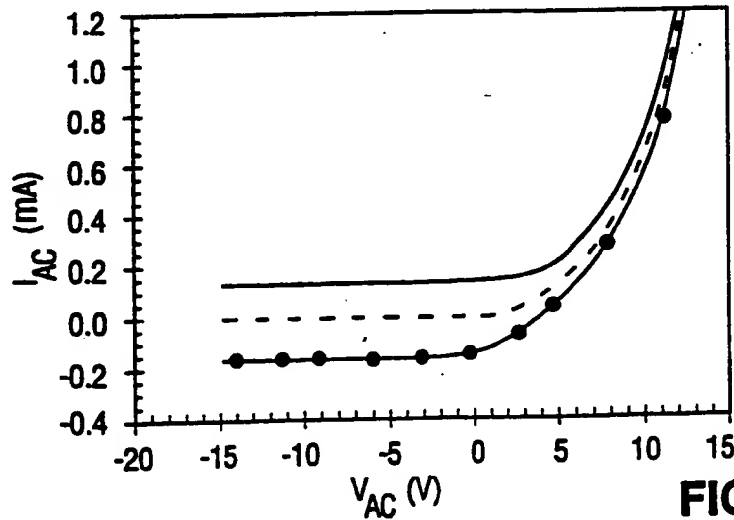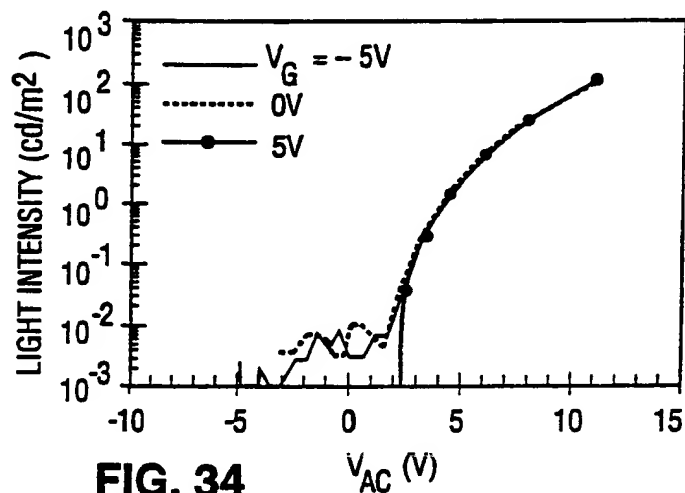
FIG. 36

FIG. 37

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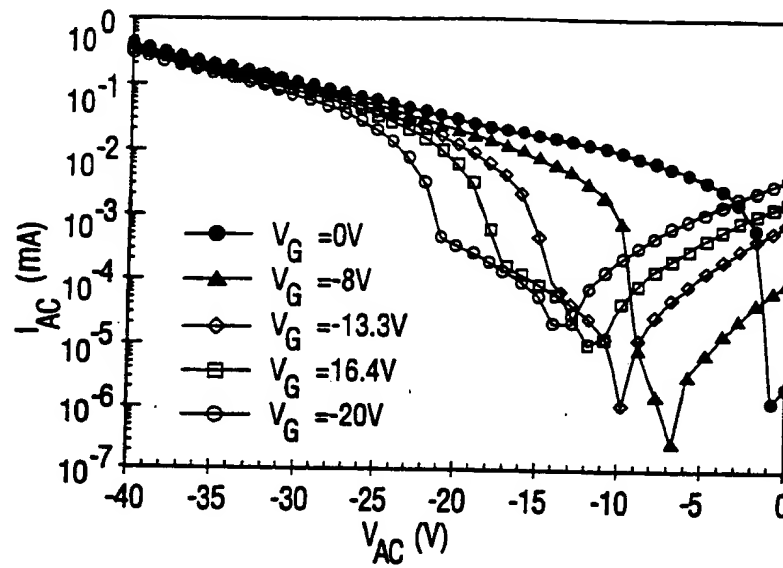
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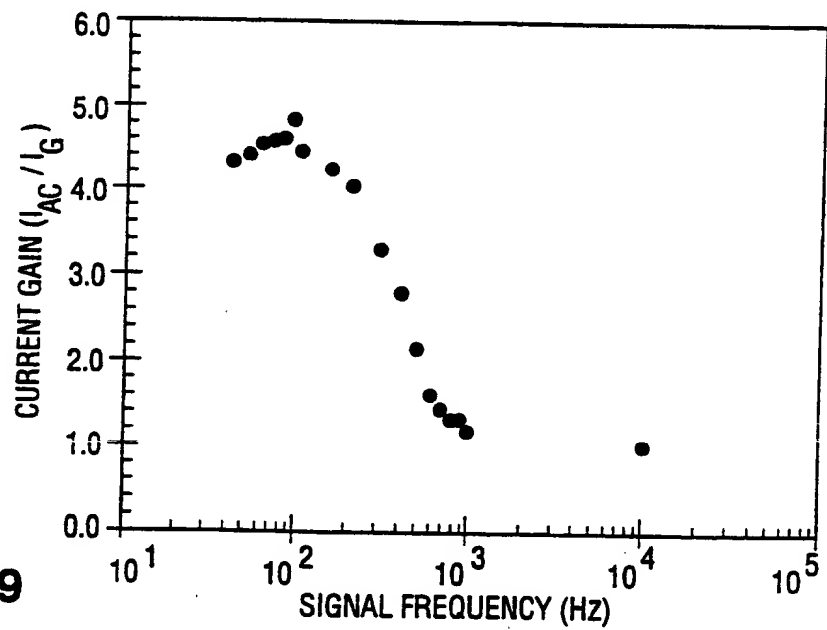
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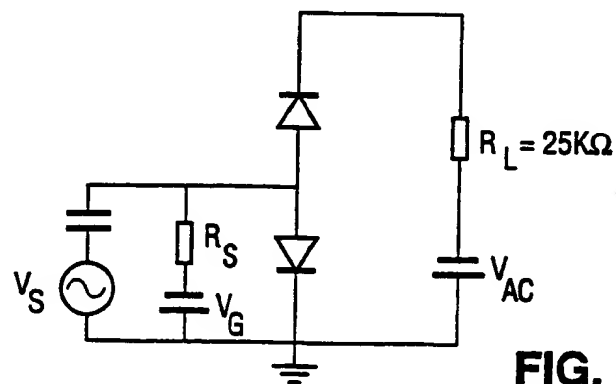
FIG. 40

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INTERNATIONAL SEARCH REPORT

A. CLASSIFICATION OF SUBJECT MATTER

IPC(6) :H01L 29/28; H01J 1/62
US CL :257/40, 103, 565, 746; 313/504; 437/1
According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

U.S. : 257/40, 103, 565, 746; 313/504; 437/1

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

APS
search terms: porous, polyaniline, polypyrrole, PPV, luminescent, electroluminescent, electrochromic

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X --- Y	US, A, 5,282,955 [LEVANTIS ET AL] 01 February, 1994, abstract, col. 2, lines 49-57, col. 3, lines 64-68, col. 4, lines 1-9, col. 5, lines 12-14.	1-3, 8, 10- 13, 18, 33-34
		4-7, 9, 14-17, 19-25, 27-28, 35-42
Y	US, A 4,750,816 [ITO ET AL] 15 June 1988, col. 8, lines 45-47.	6-7, 20-25, 37-38, 40
A	US, A, 5,232,631 [CAO ET AL] 03 August 1993	1-69

☐ Further documents are listed in the continuation of Box C.   ☐ See patent family annex.

*	Special categories of cited documents:	"T"	later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention
"A"	document defining the general state of the art which is not considered to be of particular relevance		
"E"	earlier document published on or after the international filing date	"X"	document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone
"L"	document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)	"Y"	document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art
"O"	document referring to an oral disclosure, use, exhibition or other means		
"P"	document published prior to the international filing date but later than the priority date claimed	"&"	document member of the same patent family

Date of the actual completion of the international search	Date of mailing of the international search report
03 JULY 1995	12 JUL 1995

Name and mailing address of the ISA/US	Authorized officer
Commissioner of Patents and Trademarks Box PCT Washington, D.C. 20231	SARA W. CRANE
Facsimile No. (703) 305-3230	Telephone No. (703) 308-0956

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